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<b>(21) International Application Number:</b> PCT/US98/22753 <b>(22) International Filing Date:</b> 27 October 1998 (27.10.98) <b>(30) Priority Data:</b> 60/063,959 31 October 1997 (31.10.97) US <b>(71) Applicant:</b> MONSANTO COMPANY [US/US]; 800 N. Lindbergh Boulevard, St. Louis, MO 63167 (US). <b>(72) Inventors:</b> ASRAR, Jawed; 14949 Royal Brook Drive, Chesterfield, MO 63017 (US). PIERRE, Jean, R.; Rue des Trois Bonniers 13, B-5081 St.-Denis (BE). <b>(74) Agent:</b> KAMMERER, Patricia, A.; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PLASTICIZED POLYHYDROXYALKANOATE COMPOSITIONS AND METHODS FOR THEIR USE IN THE PRODUCTION OF SHAPED POLYMERIC ARTICLES  <b>(57) Abstract</b>  Plasticized PHA pellet compositions are provided which are processible into shaped objects, particularly blown and cast free-standing films. The Mw of the PHA in the pellets used to produce the films is at least 470,000.		

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**PLASTICIZED POLYHYDROXYALKANOATE COMPOSITIONS AND  
METHODS FOR THEIR USE IN THE PRODUCTION OF  
SHAPED POLYMERIC ARTICLES**

5 This invention relates generally to biodegradable polyester compositions and in particular to high molecular weight polyhydroxyalkanoates (PHAs) containing one or more plasticizers. It also relates to the use of such compositions in the production of PHA shaped objects/articles.

**BACKGROUND OF THE INVENTION**

10 There has been considerable interest in recent years in the use of biodegradable polymers to address concerns over plastic waste accumulation. The potential worldwide market for biodegradable polymers is enormous (> 10 B lbs/yr). Some of the markets and applications most amenable to the use of such biopolymers involve those having single, short use applications, including packaging, personal hygiene, garbage bags, and others. These applications, although poorly suited for recycling, are ideally suited for  
15 biodegradation through composting.

PHA biopolymers are polyesters produced by numerous microorganisms in response to nutrient limitation. The commercial potential for PHA spans many industries, and is derived primarily from certain advantageous properties which distinguish PHA polymers from petrochemical-derived polymers and other polymers derived from  
20 renewable resources, namely excellent biodegradability and/or natural renewability compared to the petrochemical-derived polymers, and hydrophobicity compared to other polymers derived from renewable resources.

Widespread use and acceptance of PHA, however, has been somewhat hindered by certain undesirable chemical and physical properties of these polymers. For example,  
25 PHA is one of the most thermosensitive of all commercially available polymers. As such, a dramatic rate of polymer degradation is observed at the temperatures typically required for conventional processing of PHA into end-products such as films, coatings, fibers etc. An additional limitation of the potential utility of PHA polymers relates to the observation that certain characteristics such as ductility, flexibility and elongation of the polymer  
30 diminish over time. This rapid "aging" of certain PHA-derived products is unacceptable

their intended useful life. The success of PHA as a viable alternative to both petrochemical-derived polymers and to non-PHA biodegradable polymers, will depend upon novel approaches to overcome the unique difficulties associated with PHA polymer processing and with products derived therefrom.

5 Polymeric films with properties suitable for diverse applications have been difficult to prepare using PHAs due to their frequently unacceptable mechanical characteristics, for example poor melt strength, rapid aging, and brittleness.

GB 2,243,327 teaches that biodegradable PHA polymers, such as polyhydroxybutyrate-co-valerate (PHBV) copolymer, cannot be formed into thin films  
10 while maintaining the required strength and tear resistance for applications such as a diaper backsheet. This problem was addressed by combining a thin biodegradable thermoplastic polymer film into a sheet laminate with at least one layer of a fiber substrate comprised of biodegradable fibers. However, a cast film of PHBV (6.5% HV) 20 - 24 microns thick when laminated with a rayon nonwoven showed elongation at break of less  
15 than 10% in the machine direction which was less than that for the rayon portion alone.

U.S. Patent No. 4,880,592 discloses a means of achieving a free-standing PHBV film for diaper backsheet applications by coextruding the PHBV between two layers of sacrificial polymer, for example polyolefins, stretching and orienting the multilayer film, and then stripping away the polyolefin layers after the PHBV has had time to crystallize.  
20 The PHBV film is then laminated to either water soluble films or water insoluble films such as PVDC or other polyolefins.

WO 94/00293 discloses multilayer films wherein the PHBV component may be coextruded as an internal layer surrounded by outer layers of films (e.g. biodegradable films) to be used in the application (e.g. diaper films) so that the external layers are not  
25 stripped away from the PHBV layer. They remain as an integral part of a biodegradable multilayer film.

EP 736,563 describes a process for producing cast and blown films from PHBV copolymers that have been compounded with plasticizers, nucleating agents and/or other additives. No specifications of the copolymer were disclosed other than an HV content of  
30 4-16%. The molecular weights of the PHBV powder used in the examples ranged up to 520,000 before compounding and extrusion into pellets. In their disclosed process, films of

the compounded PHBV were extruded on a preformed supportive bubble of EVA-resin or LDPE with MFI less than 2.5 g/10min.

Thus, attempts to use PHAs in the production of films and other shaped objects have generally resulted in less than desirable properties. It has been difficult, for example, to develop a continuous process for film production which does not depend upon the presence of one or more non-PHA polymer layers in order to improve film processibility and/or properties. It is desired, therefore, to develop methods and compositions useful in producing PHA shaped articles having improved overall mechanical characteristics as required for the numerous applications in which resulting plastic articles are typically employed. Furthermore, it is desired that the means to produce improved PHA products be a simple and rapid process that is easily amenable to large scale production, where the PHA articles do not require the presence of non-PHA polymeric materials to achieve acceptable processing performance and/or product properties.

#### SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, there are provided pellet compositions comprising PHA, wherein the Mw of the PHA in the pellets is greater than about 470,000. The pellets are produced by melting PHA powder having a Mw greater than about 500,000, extruding a strand of the melted PHA, cooling and crystallizing the extruded strand and cutting the strands into pellets. The pellets so produced are suitable for use in the production of numerous PHA end products by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, calendered and thermoformed sheets and general extruded parts. The pellet compositions are particularly useful in the production of blown and cast free-standing films as described herein.

In accordance with another aspect of the present invention, the PHA pellet compositions include one or more plasticizers. The plasticizers can include high-boiling esters of polybasic acids; phosphoric acid derivatives; phosphorous acid derivatives; phosphonic acid derivatives; substituted fatty acids; high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified; pentaerythritols and derivatives; sulphonic acid derivatives; epoxy derivatives;

chlorinated paraffins; block copolyesters; block polyester copolyethers; and polymeric esters.

In accordance with another aspect of the present invention, there are provided blown and cast free-standing films comprising PHA which are producible by a continuous process. In order to achieve a stable film process, the Mw of the PHA in the film is preferably greater than about 420,000. Such films are produced by melting PHA, preferably in the form of the pellet compositions of the present invention, and forming the melt into a film. The films so produced have desirable melt and extensional strength characteristics. For example, they have stretch ratios between about 2 and 7, elongation to break greater than 65%, preferably greater than 75%, and tensile strength at break greater than 50 MPa, preferably greater than 75 MPa.

In accordance with another aspect of the present invention, there are provided PHA thermal stabilizers capable of inhibiting the degradation of PHA during exposure to temperatures or conditions which cause PHA degradation. The thermal stabilizers comprise compounds having the following general structure:



where R' is R or OH, and R is a branched or unbranched saturated C<sub>1</sub>-C<sub>30</sub> group, a branched or unbranched unsaturated C<sub>2</sub>-C<sub>30</sub> group, a C<sub>6</sub>-C<sub>30</sub> aromatic group, or a saturated or unsaturated C<sub>6</sub>-C<sub>30</sub> cycloaliphatic group. The compounds may contain one or more O, N or S atoms in the alkyl chains and may optionally be substituted with one or more groups selected from but not limited to hydroxyl, halo, carboxylic acid or ester, cyano, aryl, amino, hydroxylamino, mono-, di-, or trialkyl amino, phosphonic acid, etc.

Examples of suitable thermal stabilizers of this class of phosphorous-containing compounds include cyclohexylphosphonic acid, 1-cyclohexenylphosphonic acid, 1-hydroxycyclohexenylphosphonic acid, 1-hexanephosphonic acid, 1-hydroxyethylidene 1,1-diphosphonic acid, or dicyclohexylphosphonic acid, 2,4,4-(trimethylpentyl)cyclohexylphosphonic acid.

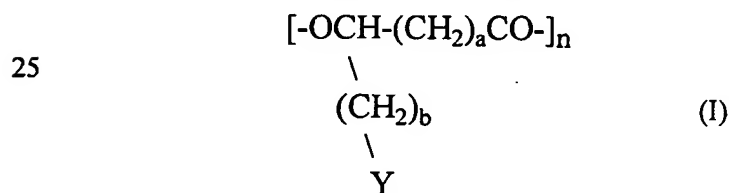
The thermal stabilizer can also comprise oxides, hydroxides, or carboxylic acid salts of a metals from Groups I to V of the Periodic Table. For example, calcium stearate, barium stearate, magnesium stearate, zinc stearate, and zinc oxide are particularly suitable for use as PHA thermal stabilizers according to the present invention. The thermal stabilizer may comprise one of the disclosed compounds or may comprise a mixture thereof.

When thermal stabilizers of the present invention are used, less PHA Mw loss is observed when compounding PHA powder into PHA pellets, and when processing PHA pellets into PHA films. As such, pellet compositions suitable for producing the PHA films of the present invention can have a PHA Mw as low as about 435,000, while still maintaining the ability to produce film having the desired Mw of greater than about 420,000. Similarly, if a thermal stabilizer is present when producing the 435,000 Mw PHA pellets from PHA powder, the Mw of the PHA powder can be as low as about 480,000.

The PHA compositions of the invention are useful for the production of polymeric objects for numerous applications. The objects can be produced, for example, by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, cast and extruded films, calendered and thermoformed sheets, general extruded parts, solution and melt spun fibers, and foamed materials and products.

#### DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

PHAs are biodegradable polymers or copolymers having the following general structure for one or more of the repeating units:



where a is 0 to 6, b is 0 to 15, Y is H, F, Cl, Br, CN, OH, CO<sub>2</sub>H, CO<sub>2</sub>R (where R is alkyl, benzyl etc.), methyl, cyclohexyl, phenyl, p-nitrophenoxy, p-cyanophenoxy, phenoxy, acetox, vinyl, 2-propyl, 2-butyl, 2-pentyl, 2-hexyl, etc., and n is an integer typically

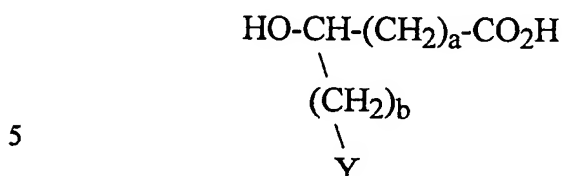
between about 10 and 25,000. The pendant groups of the repeating units may contain additional functionalization such as double bonds, epoxidized double bonds, hydroxyl groups, alkyl groups, alkenyl groups etc. or combinations thereof. The polymer main chain can contain up to 8 carbons in the repeating units and there may be additional  
5 functionalization in or on the main chain such as double bonds, alkyl groups, alkenyl groups, hydroxyl groups etc. or combinations thereof.

The PHA is preferably one capable of being biologically produced, for example in a plant or microbial organism. Most typically, it is a fermentation product, particularly of a microbiological process, whereby a microorganism lays down polyhydroxyalkanoate  
10 during normal or manipulated growth. Manipulation may be achieved by removing or failing to produce one or more nutrients necessary for cell multiplication. Numerous microbiological species are known in the art to be suitable for the production of polyhydroxyalkanoate polymers (see for example, Anderson and Dawes, Micro. Rev. 54 (4): 450-472, 1990). The microorganisms may be wild type or mutated or may have the  
15 necessary genetic material introduced into it, for example by any of the methods or recombinant DNA technology. It is to be emphasized that it is not necessary for the PHA-producing organism to be a microorganism, but at present such organisms are preferred.

The PHAs preferably have as constituents hydroxyalkanoates (HA) monomers which are substrates for PHA synthase enzymes. Biologically-produced PHA polymers  
20 are the product of PHA synthase microbial enzymes, and are produced in either a bacterial cell which naturally contains a PHA synthase, or in a bacterial or other cell type, for example a plant cell, which has been genetically engineered to express such an enzyme. The microbial PHA synthase enzymes have broad substrate ranges and are capable of incorporating a large number of HA monomers as constituents of biosynthetic PHA  
25 depending upon growth conditions, precursor substrate availability, and the source of the PHA synthase enzyme. The diversity in composition of biosynthetic PHA polymers is underscored by the fact that at least 91 HA monomers have been identified as substrates for PHA synthases (Steinbuechel, A. and Valentin, H. FEMS Micro. Letters 128 (1995) 219-228).



Suitable HA monomers can include those having the following formula:



where a is 0 to 6, b is 0 to 15 and Y is H, F, Cl, Br, CN, OH, CO<sub>2</sub>H, CO<sub>2</sub>R (where R is alkyl, benzyl etc.), methyl, cyclohexyl, phenyl, p-nitrophenoxy, p-cyanophenoxy, phenoxy, acetoxy, vinyl, 2-propyl, 2-butyl, 2-pentyl, 2-hexyl, etc. As in the above description, there may be additional functionalization in or on the pendant and/or main chains. The monomers can be homopolymerized or copolymerized either biochemically or synthetically to produce the polymer.

Preferred HA monomers include those where a= 1-4, b=0-15, and Y is H. More preferably, the monomers are those where a=1-2 and b=0-3, and Y is H.

In a most preferred polymer, the PHA is of formula (I) where a is 1, b is 1 or 2 and Y is H and especially where there are units with b = 1 and b = 2 copolymerized together. Suitable polyesters contain a preponderance of b = 1, especially with at least 70 mol % of such units, the balance being units in which b = 2. Polymer containing a = 1, b = 1, Y = H as the only units is polyhydroxybutyrate (PHB) polyester while that containing additionally b = 2 is polyhydroxy-butyrate-co-valerate (PHBV).

The polymer can also be a blend of two or more PHAs differing in the value of m. A particular example contains:

- a) polymer consisting essentially of Formula I units in which 2-5 mol % of units have a = 1, b = 2 and Y = H, the rest a = 1, b = 1, and Y = H, and
- b) polymer consisting essentially of Formula I units in which 5-30 mol % of units have a = 1, b = 2 and Y = H, the rest a = 1, b = 1, and Y = H.

The proportions of the polymer in such a blend is preferably such as to give an average a = 1, b = 2 and Y = H content in the range 2 to 28 mol % and typically 4 to 18 mol %. Thus, in a most preferred form the polymer is a poly (hydroxybutyrate/valerate) copolymer or blend of copolymers.

The compositions of the invention may contain a blend of biodegradable polyesters. Blends of particular interest are blends of PHA with polycaprolactone, polylactic acid, and cellulose esters and up to 50 % w/w of the blend preferably comprises one or more polymers selected from polycaprolactone, polylactic acid, and cellulose esters.

5 As used herein, the term "molecular weight", unless otherwise specified, refers to the weight average molecular weight (Mw) as opposed to the number average molecular weight (Mn). Most synthetic polymers have a broad distribution of molecular weights, and the molecular weights reported for such polymers represent averages, most frequently defined by Mw or Mn according to the following formulas:

$$10 \quad M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

where  $n_i$  = the number of molecules of molecular weight  $M_i$ . The most commonly used technique for determining Mw and Mn is by gel permeation chromatography (GPC). This method is capable of determining the entire molecular weight distribution of a polymer sample from which molecular weight averages can be determined. Other methods known  
15 in the art for determining Mw and Mn include osmometry, scattering and sedimentation (See for example, W. R. Sorensen & T. W. Campbell: Preparative Methods of Polymer Chemistry, Interscience Publishers, NY, 1961).

#### PHA PELLETS

For most processes that produce thermoplastic polymer products such as films and  
20 molded articles, it is desirable to have a polymer, polymer blend or polymer formulation supplied to the processor in the form of pellets. This allows the polymeric material to be provided to the processor preformulated for a particular application. In addition, the use of pellets are advantageous in that they avoid problems with dust typically encountered when handling powders. Generally, such pellets are prepared by melt extruding continuous  
25 strands of a polymer, polymer blend or the polymer formulation and then cutting the strands into pellets of a desired length.

In one embodiment of the present invention, there are provided pellet compositions comprising PHA. It has been found that pellets containing PHA of molecular weights greater than about 470,000 are extremely useful in the production of PHA films having desirable characteristics not previously observed. For example, due to the low melt strength of PHA, blown PHA films have not been successfully produced without  
5 employing the use of a supporting film. The pellet compositions of this invention allow for the production of blown and cast free-standing PHA films having excellent properties while not requiring use of a supporting film. The PHA pellet compositions have a desirably low melt flow index (MFI) less than about 20, preferably less than about 14, and  
10 more preferably less than about 8 g/10min (170° C/5 kg load).

In addition to their utility in producing PHA films as further described herein, such pellets are also useful in the production of other PHA end products by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, calendered and thermoformed sheets, general  
15 extruded parts, solution and melt spun fibers and foamed materials and products.

In a further embodiment of the present invention, there is provided a method of making the PHA pellet compositions. PHA pellets having high molecular weights have been difficult to produce due to the thermosensitivity of PHA at the processing conditions typically used in the art for pellet production. It is well known in the art that high  
20 temperatures produce very rapid PHA degradation. (See for example, Grassie, N., Murray, E. J. and Holmes, P.A.-Polym. Degrad. Stab. 6, pp. 47,95,127 (1984)). The processing conditions disclosed herein serve to minimize the thermal degradation of PHA during processing into pellets. Factors which can effect such degradation include the temperature at which extrusion is performed, the time of exposure to such temperatures, screw speed,  
25 shear heating, and screw and die design.

The pellets of this invention are generally produced by extrusion of PHA powder under conditions of low shear and temperature control, either in a single or twin screw extruder. For example, the pellets can be produced using a single screw extruder with a short barrel length ( $L/D=20$ ) and a low to medium screw speed while maintaining the melt  
30 temperature below about 170°C, cooling and crystallizing an extruded strand into a long water bath maintained at 55 to 60° C, and cutting the strand into pellets. The present

method allows for the production of high molecular weight PHA pellets without excessively compromising the stability of the polymer in response to the conditions required for their production.

5 It was unexpected that only when PHA in the pellets was of a Mw greater than about 470,000 would the pellets be processible into self-supporting blown films. The molecular weight of the PHA in the pellet compositions is determined in part by the molecular weight of the PHA powder used as the starting material to make the pellets. Thus, when making the pellets of the present invention, it is necessary to choose a suitable molecular weight of the PHA powder and to utilize appropriate processing conditions in  
10 order to arrive at pellets having the desired Mw greater than about 470,000. Under the processing conditions disclosed above and in the Examples which follow, it is typical to observe about 10 to 30 % reduction in molecular weight of the PHA in the pellets compared to the molecular weight of the PHA in the powder used to produce them. Thus, the PHA in the powder used to produce the PHA-containing pellets of the present  
15 invention typically has a Mw greater than about 500,000.

#### PLASTICIZERS

The PHA pellets of the present invention preferably contain one or more plasticizers. Plasticizers for use in the PHA pellet compositions of this invention can include those known to the skilled individual in this art, particularly those described in  
20 WO 94/28061. Such plasticizers are well suited for applications where improved impact strength and/or ductility are important.

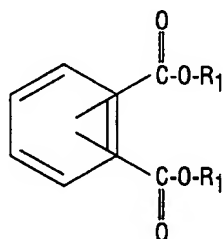
Thus, according to the present invention there are further provided PHA pellet compositions comprising at least one plasticizer selected from the group consisting of high-boiling esters of polybasic acids; phosphoric acid derivatives; phosphorous acid  
25 derivatives; phosphonic acid derivatives; substituted fatty acids; high-boiling glycols; polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified; pentaerythritols and derivatives; sulphonic acid derivatives; epoxy derivatives; chlorinated paraffins; block copolyesters; block polyester copolyethers; polymeric esters; and Wolflex-But\*. In the description, examples and claims herein a \*  
30 indicates a tradename or registered trademark.

The plasticizer is a material capable of plasticizing PHA, i.e. capable of improving the ductility of the polyester and especially a material capable of plasticizing PHB or PHBV. There may be one or more plasticizers present. For the ratio of such plasticizers to PHAs, the range up to 40 phr w/w (particularly 1 to 40 phr w/w) includes most of the likely uses and, for making effectively rigid but not brittle articles, the range 5-25 phr w/w is generally suitable.

Examples of suitable plasticizers are

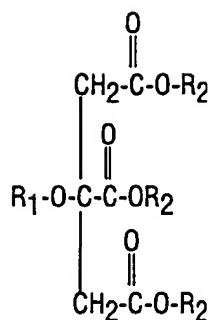
(A) high-boiling esters of polybasic acids, such as

(i) phthalates and isophthalates, particularly compounds of the formula:



where  $R_1$  is  $C_{1-20}$  alkyl, cycloalkyl or benzyl, preferably  $C_{5-11}$  alkyl, cyclohexyl or benzyl, especially isoheptyl, isoocetyl, isononyl, isodecyl and isoundecyl. For example di-isodecylphthalate (Jayflex DIDP\*), di-isooctylphthalate (Jayflex DIOP\*), di-isoheptylphthalate (Jayflex77 DHIP\*), di-baptylphthalate, di-rindecylphthalate, di-isononylphthalate (Jayflex DNIP\*), di-isoundecylphthalate (Jayflex DIUP\*), di-isodecylphthalate (Reomol DiDP\*), di-isobutylphthalate (Reomol DiBP\*) di-tridecylphthalate, butyl benzyl phthalate (Ketjenflex 160\*);

(ii) citrates; International Patent Application No. PCT/GB 93/01689 discloses a range of doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule. A particularly preferred example from that disclosure is acetyl tri-n-butyl citrate (Estaflex\*). Further citrates of the formula :



where  $\text{R}_1$  is hydrogen or  $\text{C}_{1-10}$  alkyl, and  $\text{R}_2$  is  $\text{C}_{1-10}$  alkyl,  $\text{C}_{1-10}$  alkoxy or  $\text{C}_{1-10}$  alkoxyalkyl. When  $\text{R}_1$  and  $\text{R}_2$  are alkyl each is preferably selected from straight or branched chain, methyl, ethyl, propyl, butyl, pentyl, hexyl, iso-propyl, isobutyl, or ethoxyethyl, propoxyethyl, butoxyethyl, butoxy-isopropyl and butoxyethoxyethyl are encompassed by the present invention. Particular examples are: triethylcitrate, trimethylcitrate, n-butyl tri-n-hexylcitrate (Citroflex B6), tri-n-butylcitrate (Citroflex 4).

(v) fumarates;

(vi) glutarates such as diester ether alkyl (Plasthall 7050\*);

(vii) adipates, such as those of the formula  $\text{R}_1 - \text{O} - \text{C}(\text{O}) - (\text{CH}_2)_4 - \text{C}(\text{O}) - \text{O} - \text{R}_2$  where  $\text{R}_1$  and  $\text{R}_2$  which may be the same or different are  $\text{C}_{2-12}$  alkyl (e.g. butyl),  $\text{C}_{2-12}$  alkoxyalkyl (e.g. butoxyethyl), for example, di-2-ethylhexyl adipate (Reomol DOA\*), di-isodecyl adipate, di-isononyl adipate, dioctyl adipate; other esterified radicals may be for example  $\text{C}_1 - \text{C}_{12}$  alkyl, aryl, or aralkyl.

(viii) sebacates of the formula  $\text{R}_1 - \text{O} - \text{C}(\text{O}) - (\text{CH}_2)_8 - \text{C}(\text{O}) - \text{O} - \text{R}_1$  where  $\text{R}_1$  is  $\text{C}_{2-15}$  alkyl or  $\text{C}_{2-15}$  alkoxyalkyl, for example, di-octyl sebacate, di-dodecyl sebacate, di-butoxyethyl sebacate, or di-n-butyl sebacate;

(ix) azelates of the formula  $\text{R}_1 - \text{O} - \text{C}(\text{O}) - (\text{CH}_2)_7 - \text{C}(\text{O}) - \text{O} - \text{R}_1$  where  $\text{R}_1$  is  $\text{C}_{2-12}$  alkyl, benzyl, or  $\text{C}_{2-12}$  alkoxy-alkyl, for example, di-n-butyl azelate and di-i-octyl azelate;

(B) high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified:

(i) high molecular weight glycols such as triethylene glycol diacetate (Estol 1593\*), triethylene glycol caprylate (Plasthall 4141\*), alkyl ethers/esters of general formula

- $R_2-(O-CH_2-CH_2)_n-O-R_1$  where  $R_1$  is alkyl or  $-C(O)$ -alkyl,  $R_2$  is alkyl and  $n$  is 2 to 100, for example Morton TP90B\* where  $R_2$  is  $C_4H_9-$  and  $n$  is 2, Reomol BCD or BCF where  $R_1$  is  $-C(O)$ -alkyl,  $R_2$  is  $C_4H_9-$  and  $n$  is 2, Morton TP759\* where  $R_2$  is  $C_4H_9-$ ,  $n$  is 2 and  $R_1$  is  $[-C(O)]_2$ -alkyl in the form of a residue of adipic acid, compounds of such formula where  $R_1$  is  $-C(O)-C_mH_{2n+1}$ , particularly up to  $m = 20$ , e.g. lauryl when  $m$  is 12, palmitate when  $m$  is 15 or oleate when  $m$  is 15 and unsaturated, stearyl when  $n$  is 17,  $R_2$  is sorbitan and  $n$  is up to 20, for example Tween 80 in which  $R_2$  is sorbitan monooleate,  $R_1$  is lauryl and  $n$  is 20; and such compounds containing irregularly spaced ether linkages, for example the compounds of the formula above in which  $R_1$  is hydrogen,  $R_2$  is alkylphenyl where the alkyl is  $C_{2-12}$  alkyl, and  $n$  is 2 to 100, for example, Igepal CA210\* where the alkyl is  $C_8$  alkyl and  $n$  is 2, Igepal CA510\* which is the same as CA210 except that  $n$  is 5, Triton X-100\* and Triton X-405\* which is the same as Igepal CA510\* except that  $n$  is 10 and 40 respectively, Plasthall CPH27N, CPH30N and CPH39 where  $R_1$  is hydrogen,  $R_2$  is  $CH_3-(CH_2)_{10}-C(O)-$  and  $n$  is 10, 5 and 15 respectively, Plasthall CPH39N and CPH41N in which  $R_1$  is hydrogen,  $R_2$  is  $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-C(O)-$  and  $n$  is 5 and 15 respectively; PEG 2000, PEG 6000 and PEG 10000 where  $R_1$  and  $R_2$  are both hydrogen and  $n$  is 50, 150 and 200 respectively;
- (ii) examples of polyglycols are poly(propylene glycol) (PPG 100\*, PPG 725\*, PPG 425\*), poly(ethylene) glycol (PEG 300\*, PEG 200\*);
  - (iii) examples of glycerol derivatives are glycerol tricaprolate, glycerol tributyrates;
  - (iv) pentaerythritols and derivatives;

The acid-derived radical of the ester typically contains 2-10 carbon atoms.

- (C) sulphonic acid derivatives such as toluenesulphonamide (Ketjenflex 15\*, Ketjenflex 8\*, Ketjenflex 7\*, Ketjenflex 3\*);
- (D) epoxy derivatives such as the compounds of formula  $CH_3-(CH_2)_n-A-(CH_2)_n-R$  in which the A is an alkene containing one or more double bonds (i.e. unsaturated fatty acids),  $n$  is up to 25 and R is  $C_{2-15}$  alkyl, or epoxy derivatives of triglycerides containing one or more double bonds per fatty acid chain with chain lengths from  $C_{6-26}$ , such as epoxidized soya bean oil, epoxidised linseed oils, epoxidised octyl

- tallate, epoxidised glycololeate, e.g. Lankro EDG\*, Lankro GE\*, Paraplex G60\*, Paraplex G62\*, Plasthall E50\*, Rheoplas 39\* and Lankro L\*;
- (E) substituted fatty acids such as palmitates, stearates, oleates, ricinoleates and laurates, for example, sorbitan monolaurate, sorbitan monooleate, poly(oxyethylene)(20)Sorbitan monolaurate (Tween 20\*), poly(oxyethylene)(4)lauryl ether (Brij 30\*), butyl acetyl ricinoleate (BAR\*);
- (F) phosphoric acid derivatives (phosphates), particularly compounds of the formula  $O = P(OR)_3$  where R is straight chain or branched  $C_{1-25}$  alkyl, alkoxyalkyl (e.g. ethylene oxide chains, propylene oxide chains with 2 to 30 repeat units), phenyl, or phenylalkyl where the alkyl is straight chain or branched  $C_{1-25}$ , for example, isopropyl-phenyl. Particular examples are: phosphate ester (Reomol 249\*), tri-isopropyl phenyl phosphate (Reofos 95\*); and phosphonic acid derivatives and phosphites;
- (G) chlorinated paraffins such as Cereclor 56L\*, Cerechlor 552\*;
- (H) polymeric esters such as those of the formula  $-O-C(O)-R_1-C(O)-O-R_2-O-$  in which  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene,  $R_2$  may be derived from a diol such as 1,2-propanediol, 1,3 butanediol, 1,4-butanediol or 1,6-hexanediol; for example;
- (i) polyester glutarates having molecular weights from 2000 to 20,000, e.g. Plasthall 550\*, Plasthall 7046\*, Plasthall 7092\* Paraplex P550\*, Paraplex P7035\*;
- (ii) polyester adipates having a molecular weight from 200 to 20000, for example, Plasthall 643\*, Plasthall 650\*, poly(propylene) adipate for example LANKROFLEX PLA\*, LANKROFLEX PPL\*, LANKROFLEX PPA/3\*, Paraplex G56\*, Paraplex G59\* Diolpate 214\*, and Diolpate 917\*, poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer\*S409A; Mw = 3700, available from Solutia Inc.), poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer\*S433; Mw = 3500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) unterminated (Santicizer\*S430; Mw = 2500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) unterminated (Santicizer\*S421; Mw = 1250, available from Solutia Inc.), poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer\*S438; Mw = 1900, available from Solutia



- Inc.), poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol (Santicizer \*S435; Mw = 2500; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer \*431; Mw = 1200; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2 ethylhexanol (Santicizer \*S4212; Mw = 950; available from Solutia Inc.), poly (1,3-butylene glycol adipic acid) terminated with mixed fatty acids (Santicizer \*S405; Mw = 2000; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer\* S436; Mw = 3500; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer \*S449; Mw = 3700; available from Solutia Inc.), poly(1,4-butylene glycol adipic acid), or poly(1,4-butylene glycol-co-ethylene glycol adipic acid).
- (iii) succinic polyesters;
  - (iv) sebacic polyesters having a molecular weight from 4000 to 10000, preferably 8000, for example, Plasthall 1070\*;
  - 15 (iv) Diolpate OL1696\*, Diorex 570\*;
  - (v) lactone copolymers of the formula  $[-(O-C(O)-R_1-C(O)-O-R_2-O)]_m [-C(O)-R_3-O]_n$ , where  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene, or  $R_2$  may be derived from a diol such as 1,2-propanediol, 1,3butanediol, 1,4-butanediol or 1,6-hexanediol, and  $R_3$  is  $-(CH_2)_5-$  (based on caprolactone);
  - 20 (vi) polyesters such as Reoplex 346\*, Reoplex 1102\*, Reomol MD (ester of mixed adipic, glutaric and succinic acids with isodecanol), polycaprolactone triol (PCL Triol (300)\*);
  - (I) Wolflex-But\*;

Preferred plasticizers are the polymeric esters, high-boiling glycols, polyglycols, 25 polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified, epoxidised soyabean oils, adipates, sebacates, phosphate esters, phthalates, citrates, castor oil, chlorinated paraffins and toluene sulphonamide derivatives.

Plasticizers which are particularly preferred for conferring improved impact properties are high molecular weight glycols of general formula  $R_2-(O-CH_2-CH_2)_n-O-R_1$ ,

for example Reomol BCD; adipates, for example di-isodecyl adipate; mixed polyesters, for example Reomol MD; polyester glutarate, for example Paraplex 550; and citrates.

Particularly preferred polymeric esters are adipic esters, such as poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol  
5 (Santicizer\*S409A; Mw = 3700, available from Solutia Inc.), poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer\*S433; Mw = 3500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) unterminated (Santicizer\*S430; Mw = 2500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) unterminated (Santicizer\*S421; Mw = 1250, available from Solutia Inc.),  
10 poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer\*S438; Mw = 1900, available from Solutia Inc.), poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol (Santicizer \*S435; Mw = 2500; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer \*S431; Mw = 1200; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2 ethylhexanol  
15 (Santicizer \*S4212; Mw = 950; available from Solutia Inc.), poly (1,3-butylene glycol adipic acid) terminated with mixed fatty acids (Santicizer \*S405; Mw = 2000; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer\* S436; Mw = 3500; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer \*S449; Mw = 3700; available from Solutia Inc.), poly(1,4-butylene glycol adipic acid), or poly(1,4-butylene glycol-co-ethylene glycol adipic acid).

The composition may contain one or more plasticizers selected from those defined herein and may additionally contain one or more plasticizers previously known to  
25 plasticize polyhydroxyalkanoates, for example, citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate.

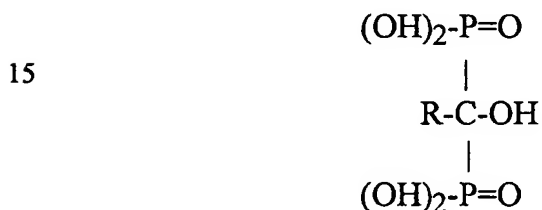
The compositions of the invention can additionally contain the usual polymer processing additives such as fillers, fibers, nucleants, and pigments such as titanium  
30 dioxide. It can be in the form of moldings, extrudates, coatings, films or fibers, including multilayer coatings, films or fibers.

Because many of the above plasticizers provide improved elongational properties that can be better sustained over time than the properties of non-plasticized materials, intermediate forms of the plasticized compositions, such as sheets and films, are advantageous since they would retain sufficient properties for forming into final products  
 5 over a period of several months.

### NUCLEANTS

Nucleants are also typically used in producing the PHA pellets of the present invention. Suitable nucleants can be selected from those known in the art, for example  
 10 particulate nucleants such as saccharin, talc, boron nitride, ammonium chloride, PHB seed crystals, "polymer soluble" nucleants such as organic phosphonic acids and their combinations with stearic acid salts (see for example WO 91/19759).

A preferred nucleant is one having the following structure:



20 where R can be hydroxy, hydrogen, C1-C25 alkyl groups (with or without one or more substituent groups such as -OH, -CO<sub>2</sub>H, -Cl, -Br, -NH<sub>2</sub>, -N(alkyl)H or N(alkyl)<sub>2</sub>), cycloalkyl groups, aryl or arylalkyl groups (such as phenyl, benzyl, etc. with or without substituents on the aromatic rings). Synthesis of such compounds can be achieved, for example, by reaction of organocarboxylic acids, PCl<sub>3</sub> in an aqueous medium. The  
 25 compounds and their syntheses have been described in the prior art for use as water treating chemicals, detergent ingredients, etc. (for example see U.S. 3,855,284, U.S. 3,400,147, U.S. 3,400,150, U.S. 4,254,063, Aus. 599,950, FR 1,521,961 and CA 93:182031). The synthesis can also be applied to dibasic acids such as adipic acid, succinic acid, etc. to give the corresponding tetrakis phosphonic acid (i.e., di-ODPAs) which can  
 30 also be used as nucleants. For example, with adipic acid, 1,6-dihydroxy-1,6-dihexanediylidene tetraphosphonic acid is obtained (Aus. 599950). Other compounds that

can be used as nucleants include methylene diphosphonic acid (PL 131549) and carbonyl diphosphonic acid (CA 93:182031). Such compounds are herein sometimes referred to as organodiphosphonic acids or ODPAs, which is term intended to include both ODPAs and di-ODPAs. The ODPAs may also be formed in situ, for example by reaction of the corresponding phosphinic acid.

Preferred ODPAs include 1-hydroxy-lower alkylidene-1,1-diphosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), 1-hydroxypropylidene-1,1-diphosphonic acid, 1-hydroxybutylidene-1,1-phosphonic acid, 1-hydroxycyclohexylidene-1,1-diphosphonic acid. In a most preferred nucleant, both acid moieties are phosphonic acid moieties, R1 is a methyl group and R2 is hydroxy group (i.e., HEDP). HEDP is available as a mixture of HEDP in water from Monsanto Company (800 N. Lindbergh, St. Louis, MO 63167) under the tradename DEQUEST 2010. The ODPAs are used in amounts typically in the range of 0.01 - 5.0 phr (parts per hundred resin), more preferably about 0.02 - 1.0 phr, most preferably 0.02 - 0.5 phr.

The nucleants can further be metallic salts of ODPAs, preferably mono-metallic salts. However, it is generally preferred that not all, e.g., less than 70%, more preferably less than 60% of the phosphonic acid moieties are involved in the salt formation since it has been found that excessive salt formation may adversely influence the effectiveness of certain nucleants of the invention.

Organic metal salts and/or certain inorganic compounds can be used to further improve nucleation activity and/or reduce the extent of discoloration and/or improve the clarity of PHA-derived products when used in combination with the ODPAs of the invention. The organic metal salt is preferably an organic acid salt, more preferably a fatty acid metal salt. The inorganic compound is preferably an metal oxide, a metal hydroxide or a metal carbonate. Suitable metals include those selected from Groups I to V of the periodic table, preferably aluminum, antimony, tin, sodium, calcium, magnesium, barium or zinc. Most preferably the metal is one which has benign environmental and toxicological properties such as magnesium, calcium and barium. Preferred fatty acids include stearic acid, palmitic acid, acetic acid, propionic acid, caproic acid, oleic acid, behenic acid and montanic acid. Most preferably, the fatty acid metal salt of the invention is calcium stearate or magnesium stearate which have proven highly effective in

combination with ODPAs in nucleating thermoplastic polyesters. The organic metal salt or the inorganic metal oxide, metal hydroxide or metal carbonate is used in an amount typically ranging from 0.001 to 5 phr (parts per hundred of resin), preferably about 0.005 to 2 phr, and most preferably about 0.01 to 0.5 phr.

5           A nucleant formulation preferably comprises organic metal salt (or inorganic metal oxide, metal hydroxide or metal carbonate) and ODPA in weight ratios of about 0.01:1 to 10:1, preferably about 0.05:1 to 7.5:1, and more preferably about 0.1:1 to 5:1. When calcium stearate is used in a preferred nucleant formulation, a 3:1 ratio has been found to provide a suitable solid support for the ODPA-solvent solution and to produce a PHA  
10   nucleant with desirable activity.

          The weak organic base is one which is effective in improving the elongational properties and/or clarity of the polymeric material. The weak organic base should be polymer-miscible or -soluble and melt at a sufficiently high temperature so that, if desired, nucleating agent solvent can be readily removed during preparation. The weak organic  
15   base preferably comprises a mono-, bis-, or tri- fatty acid amide, as these generally exhibit good hydrolytic stability in the presence of ODPAs. More preferably, the weak organic base is a stearamide, for example ethylene bistearamide (EBS), available from Lonza or Henkel under the tradename Acrawax C or Loxamid EBS. The weak organic base is typically present in the polymeric compositions in an amount between about 0.01 to 9.0  
20   phr, preferably between about 0.05 to 1.0 phr, most preferably about 0.1 to 0.5 phr.

          One nucleant system that can be used comprises phosphonate/calcium stearate/EBS present in ratios effective for nucleating PHA and producing PHA articles having excellent clarity, color, elongational and tensile properties. This system is soluble in the polymer and also stabilizes PHA against thermal degradation. The phosphonates that can be used  
25   include those described as phosphorous-containing compounds under "PHA Thermal Stabilization" below. This nucleant system is especially suitable for nucleating PHBV to obtain a clear composition for use as a film.

          A most preferred nucleant for use in this invention comprises HEDP/calcium stearate/EBS present in ratios effective for nucleating PHA and producing PHA articles  
30   having excellent clarity, color, elongational and tensile properties. Most preferably, the

constituents of this formulation are present in weight ratios of about 0.8/1.5/1.7 respectively.

Suitable levels of such a nucleant formulation to be added to the PHA range from about 0.01 to 5.0 parts per hundred of resin (phr). Preferably, the level of the nucleant  
5 formulation is about 0.05 - 1.0 phr, and most preferably it is about 0.1 - 0.6 phr.

It is advantageous when preparing the nucleant to dissolve/suspend the ODPAs, and optionally the organic metal salt, inorganic metal oxide, metal hydroxide or metal carbonate, and/or the weak organic base, in an effective nucleating agent solvent. Preferably, the solvent is then removed, for example by evaporation under vacuum, giving  
10 rise to solids which are ground, pulverized, or otherwise treated so as to produce particles with diameters less than about 710 microns, preferably less than about 350 microns. The term "effective nucleating agent solvent" herein means a solvent which dissolves the ODPAs and preferably enhances its nucleation activity but which does not intolerably reduce its effectiveness as a nucleant. Thus, the ODPAs prepared using an effective  
15 nucleating agent solvent as described herein will have at least as effective nucleation activity, preferably greater nucleation activity, compared to the same ODPAs that is not dissolved in an effective nucleating agent solvent during its preparation or use.

Nucleating agent solvents for use in this invention include but are not limited to C1 to C6 aliphatic mono, di- and tri- ols such as methanol, ethanol, ethylene glycol, 1- or 2-  
20 propanol, propylene glycol, glycerol, 2-methyl-2-propanol, 2-butanol and the like, and further including mixtures of such solvents with each other and with water. Preferred nucleating agent solvents include methanol, ethanol or another lower alcohols, or mixtures of such alcohols with water to allow for easy solvent removal. The nucleating agent solvent needs to be appropriately selected since it has been found that some solvents such  
25 as acetone and tetrahydrofuran when used with some ODPAs such as HEDP are not effective nucleating agent solvents. However, it is known that mixtures of solvents, e.g. methanol and acetone, can serve as effective nucleating agent solvents as defined herein even though one of the solvents in the mixture is not an effective nucleating agent solvent when used alone. While all of the solvents which will be effective nucleating agent  
30 solvents has not yet been elucidated, a person skilled in the art can readily determine

whether a proposed solvent for an ODPA is "effective" by routine experimentation following the description herein.

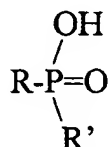
It would be understood by one skilled in the art that the PHA pellet compositions of the present invention may include a number of additives or other components which are commonly included in polymeric materials without departing from the spirit and scope of the present invention. These may include, for example, dyes, fillers, stabilizers, modifiers, anti-blocking additives, antistatic agents etc.

#### PHA THERMAL STABILIZATION

In another embodiment of the present invention, there is provided a means for further minimizing the thermal degradation of PHA. It has been found that the presence of certain compounds, hereinafter referred to as thermal stabilizers, can reduce the extent of molecular weight loss due to PHA degradation normally observed during compounding of PHA powder into PHA pellets, and during processing of PHA pellets into end products such as films. Given the extreme thermosensitivity of PHA, the present method is applicable to any situation where it is desirable to minimize PHA degradation during exposure to temperatures or other conditions which would typically cause such degradation.

Thermal degradation of PHA is generally believed to take place by chain scission involving the formation of a six-membered transition state. Unlike most polymers, where thermal degradation is a free radical process, it has been reported and generally accepted that free radical scavengers and known thermal stabilizers have not been effective in stabilizing PHA against thermal degradation.

One class of thermal stabilizers of the present invention comprise compounds having the following structural formula:



where R' is R or OH, and R is a branched or unbranched saturated C<sub>1</sub>-C<sub>30</sub> group, a branched or unbranched unsaturated C<sub>2</sub>-C<sub>30</sub> group, a C<sub>6</sub>-C<sub>30</sub> aromatic group, or a

saturated or unsaturated C<sub>6</sub>-C<sub>30</sub> cycloaliphatic group. The compounds may contain one or more O, N or S atoms in the alkyl chains and may optionally be substituted with one or more groups selected from but not limited to hydroxyl, halo, carboxylic acid or ester, cyano, aryl, amino, hydroxylamino, mono-, di-, or trialkyl amino, phosphonic acid, etc.

5        Examples of suitable thermal stabilizers of this class of phosphorous-containing compounds include cyclohexylphosphonic acid (DZB), 1-cyclohexenylphosphonic acid, 1-hydroxycyclohexenylphosphonic acid, 1-hexanephosphonic acid, 1-hydroxyethylidene 1,1-diphosphonic acid, or dicyclohexylphosphonic acid, 2,4,4-(trimethylpentyl)cyclohexylphosphonic acid. Particularly useful are cyclohexylphosphonic  
10 acid and 1-hydroxyethylidene-1,1-diphosphonic acid.

The present findings suggest that, although random chain scission is likely the main mode of thermally induced PHA degradation, other processes such as thermo-oxidative degradation may also be operative in reducing the Mw of PHA during thermal processing since phosphorous-containing compounds can act as oxygen scavengers.

15        Various metal containing compounds can also serve as PHA thermal stabilizers. Metal compounds suitable for use in the present invention include oxides, hydroxides, and saturated or unsaturated carboxylic acid salts of metals from Groups I to V of the Periodic Table. These can include, for example, compounds of aluminum, antimony, barium, tin, sodium, calcium, magnesium and zinc. The carboxylic acids can include stearates and  
20 palmitates. Particularly useful are fatty acid salts such as calcium stearate (CaSt), magnesium stearate (MgSt), zinc stearate (ZnSt), and zinc oxide. While not wishing to be bound by this explanation, it is possible that the ability of such compounds to act as thermal stabilizers may be due to their lubricating effects. This may result in reduced shear heating generated during processing, thereby resulting in less internal polymer heat  
25 and therefore less degradation.

A single thermal stabilizer may be used in an amount sufficient to inhibit PHA degradation. Alternatively, a combination of thermal stabilizers can be used. In one preferred embodiment, both DZB and zinc stearate are dry blended with the PHA powder used to produce PHA pellets. Although a DZB/ZnSt combination has been used as a  
30 nucleant system in some settings (see for example WO 91/19759) the ability of such compounds to act as thermal stabilizers for PHA has not been previously recognized. This



invention demonstrates that the presence of DZB and ZnSt results in significantly less PHA degradation during the pellet forming process. As a result, PHA pellets extruded with DZB and ZnSt show significantly less molecular weight loss relative to the PHA powder used to produce them than PHA pellets extruded with the commonly used nucleant, boron nitride. Furthermore, when these pellets are melt processed into films, significantly less Mw reduction during film production is observed, as further described below.

### SHAPED PHA ARTICLES

The compositions of the invention are especially useful for making shaped articles such as films, especially for packaging, fibers, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

In a preferred embodiment of the present invention, there are provided PHA film compositions. Extruded PHAs having molecular weights greater than about 420,000 provide a novel and desirable combination of melt strength during initial film formation and subsequent drawability sufficient for use in stable blown film and cast film processes.

The differences in properties for films containing PHA having molecular weights less than about 420,000, compared to films containing PHA of higher molecular weights was unexpected. It was further unexpected that even higher molecular weight PHA films (i.e. greater than 420,000) could be produced without encountering processing difficulties due to unacceptably high viscosities. Polymer melt having desired melt and extensional strengths, while maintaining good processibility, were only achieved when the molecular weight of the PHA in the extruded film was greater than about 420,000.

The PHA film compositions of the present invention are preferably oriented, either mono- or bi-axially, in order to maximize mechanical properties. Bi-axially oriented means to stretch the film along a direction in which it travels, called the machine direction, and in a direction 90° to the machine direction in the plane of the film, known as the transverse direction, thereby extending length and width of the film to greater than its initial dimensions. Bi-axial orientation may involve simultaneous or sequential stretching. Mono-axial orientation refers to stretching in either the machine direction or the transverse

direction, but not both. PHA film compositions of the present invention are formed into films of a uniform thickness ranging from about 75 to 150 microns prior to orientation, and ranging from about 5 to 100 microns after orientation.

Films of the present invention typically exhibit elongation to break greater than  
5 65%, preferably greater than 75%, and more preferably greater than 100%. In addition, the tensile strength of the films is typically greater than 50 MPa, preferably greater than 75 MPa, and more preferably greater than 90 MPa.

In a further embodiment, there is provided a method of significantly reducing PHA molecular weight loss during polymer processing into a shaped object by providing one or  
10 more thermal stabilizers of the present invention. For example, the presence of DZB and ZnSt in the pellets used to produce the films of the present invention resulted in only a 3% PHA Mw loss during film processing compared to 14.1% when boron nitride was used as a nucleant (see Example 21). Thus, when thermal stabilizers are present in the pelletized PHA, the molecular weight of the PHA in the pellet can be as low as about 435,000 while  
15 still allowing for the production of blown film containing PHA of the desired molecular weight greater than about 420,000.

It would be understood by one skilled in the art that the PHA film compositions of the present invention may include a number of additives or other components which are commonly included in polymeric films without departing from the spirit and scope of the  
20 present invention. These may include, for example, dyes, fillers, stabilizers, modifiers, anti-blocking additives, antistatic agents etc.

The PHA film compositions of the present invention are useful for numerous applications involving packaging, bags and/or membranes. The films are particularly well suited for production of food and non-food packaging, protecting films, trash bags, blisters, slit film woven bags, composting bags, shopping bags and bubble films.  
25

In addition to susceptibility of PHAs to thermal degradation, low melt strength and slow crystallization rates further complicate film processing methods. Low polymer melt strength creates a need to operate cast film lines at slow line speeds or to use a supporting film or web onto which the PHBV is cast and later isolated as a free-standing film by  
30 peeling away the supporting film. Low melt strength makes it extremely difficult to produce blown film without the use of a supporting blown film. Additionally, when

producing blown films, residual tack of the PHA can cause the tubular film to stick to itself after it has been cooled and collapsed for winding.

In a further embodiment which overcomes many such limitations, there is provided a process for producing PHA films. Previously, a continuous process for the production of blown and cast free-standing PHA film has been difficult to develop due in part to poor melt strength of the material. The method involves melt processing PHA, preferably in the form of the PHA pellets of this invention, forming the melt into a film, for example by blowing a bubble through a circular die or by casting on cooling rolls through a T shape flat die, and orienting the film by continuous mono- or bi-axial stretching. The Mw of the PHA in the film is greater than 420,000. The Mw of the PHA in the pellets used to produce the film will depend whether PHA thermal stabilizers are present. If none are present, the PHA in the pellets preferably has a molecular weight greater than about 470,000. If PHA thermal stabilizers are present in accordance with the present invention, the Mw of the PHA in the pellets can be as low as about 435,000 while still being suitable for producing film containing PHA of the desired Mw greater than about 420,000.

The films of the present invention can be formed by a variety of known techniques, such as extrusion processes including calendering, flat die extrusion and film blowing, in addition to casting solutions or suspensions of polymeric compositions followed by solvent recovery.

This method has been found to be particularly useful in producing blown and cast free-standing films having molecular weights greater than 420,000. Many polymer materials used for industrial and agricultural applications are produced from blown and cast film. However, PHA pellets processible into unsupported film by this approach have been neither described nor characterized as having that capability.

In accordance with the present invention, there is provided a stable film blowing process capable of producing unsupported blown PHA films. The molecular weight of the PHA in the pellets is critical in achieving a stable film blowing process in accordance with this method. PHA pellets having molecular weights less than about 470,000, or less than about 435,000 if PHA thermal stabilizers are present, are not suitable for the production of blown films due in part to bubble instability caused by low melt strength.

Film blowing processes are well known in the art (see for example Rosato & Rosato, Plasticizer Processing Data Handbook. Van Nostrand Reinhold (Pub.), NY, 1990). Film blowing typically involves melt extrusion of a tubular preform, cooling the preform, blowing the preform with air such that a stable bubble is formed, collapsing the bubble  
5 between nip rolls to produce a film. During blown film processing, the blow up ratio determines the amount of circumferential orientation and the pull rate of the bubble determines longitudinal orientation. With PHA films, mono orientation can be achieved by operating with a puller roll speed to feeder roll speed sufficient to give a draw ratio in the 2-6 range. The cooling rate (air flow), thickness, diameter and height of the bubble are  
10 adjusted so that the PHA tubular film is sufficiently crystalline to produce orientation and prevent sticking and blocking, but not too crystalline so as to exhibit undesirable stiffness and brittleness which would prevent the continuous drawing operation.

In orienting film or sheet, a tentering frame may be used which has continuous speed control and diverging tracks with holding clamps. As the clamps move apart at  
15 prescribed diverging angles, the hot plastic is stretched in the transverse direction resulting in monodirectional orientation. To obtain bidirectional orientation, an in-line series of heat controlled rolls are located between the extruder and tenter frame. The rotation of each succeeding roller can be increased depending upon the longitudinal stretched properties desired.

20 The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute examples of preferred modes for its practice. However, those of skill in the art should, in light of the  
25 present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

#### EXAMPLES 1-6: COMPOUNDING CONDITIONS FOR PHA PELLETS OF DIFFERENT MOLECULAR WEIGHTS

## EXAMPLES 1-3: BETOL LABORATORY EXTRUDER:

The equipment used in conjunction with these Examples included a Pappenmeier high speed mixer to prepare powder blends, a vibrating feeder allowing powder blends to be fed into the hopper of a 25 mm single screw diameter Betol extruder (L/D=20) fitted with a 4 mm diameter single strand circular die. The extruded strand was cooled and crystallized in a 5 meter long water bath held at 50 to 60°C using a thermoregulator and then cut into cylindrical pellets with 2-4mm diameter and 3-6mm length in a pelletizer.

Table 1 : Compounding temperatures profiles: (°C)

	BARREL			DIE
	T1	T2	T3	T4
A:	140	150	150	155
B:	140	150	160	160
C:	140	160	170	170
D:	150	170	180	180
E:	160	180	190	190
F:	170	190	200	200

## EXAMPLE 1

PHA pellets were compounded from formulations based on BIOPOL powder (available from Monsanto Company) of Mw=744k, 1 phr boron nitride (BN) and 10 phr acetyltributylcitrate (ATC) plasticizer. BIOPOL powder comprises polyhydroxybutyrate-co-valerate (PHBV) copolymer having 8% valerate. Melt flow index (MFI) values were determined at 170 C and 5 kg load. The powder blends prepared in a Pappenmeier high speed blender were fed in a Betol single screw, using the conditions summarized in Tables 1 and 2. BIOPOL pellets with Mw's varying from 445k to 626k were obtained with output from 1.9 to 3 kg/hr depending on the screw speed used. Mw determinations for all Examples were by GPC using standard monodisperse polystyrene calibrants in a molecular weight range from 5000 to 2,250,000. The following results were obtained:

Table 2: Compounding conditions-from BIOPOL powder Mw=744k:

5	NUCL	TEMP.SCREW	Mw	Mw	MFI	OUTPUT
		PROFILE (see Table 1)	SPEED (rpm)		/Mn (g/10min)	(kg/hr)
10	BN	C	40	626k	2.4	2.4
	BN	D	60	574k	2.4	4.3
	BN	E	40	537k	2.6	6.6
	BN	F	40	445k	2.9	14.4

## EXAMPLE 2

PHA pellets were compounded from formulations based on BIOPOL powder of Mw=895k, 1 phr BN and 10 phr ATC plasticizer. Plasticizer were determined at 170°C and 5 kg load. The powder blends prepared in a Pappenmeier high speed blender were fed in a Betol single screw extruder, using the conditions summarized in the Tables 1 and 3. BIOPOL pellets with Mw varying from 625k to 796k were obtained with output from 2.9 to 4.7 kg/hr depending on the screw speed used. The following results were obtained:

20	Table 3: Compounding conditions from BIOPOL powder Mw=895k:						
25	GRADE	TEMP. PROFILE (see Table 1)	SCREW SPEED (rpm)	Mw	Mw/Mn	MFI (g/10min)	OUTPUT (kg/hr)
30	BN	A	40	796k	2.8	2.0	2.9
	BN	B	60	706k	2.7	2.5	4.7
	BN	C	40	690k	2.7	2.5	2.9
	BN	D	40	625k	2.6	3.9	3.0

## EXAMPLE 3

PHA pellets were compounded from formulations based on BIOPOL powder of Mw=895k, 0.1 phr DZB (cyclohexylphosphonic acid), 0.4 phr ZnSt (zinc stearate) and 10 phr ATC plasticizer. Plasticizer were determined at 170 C and 5 kg load. The powder blends prepared in a Pappenmeier high speed blender were fed in a Betol single screw extruder, using the conditions summarized in Tables 1 and 4. BIOPOL pellets with Mw of

727k were obtained with output from 3.0 kg/hr at a screw speed of 40 rpm. The following results were obtained:

Table 4: Compounding conditions from BIOPOL powder Mw=895k:

GRADE	TEMP. SCREW PROFILE (see Table 1)	Mw SPEED (rpm)	Mw	MFI /Mn	OUTPUT (g/10min)	(kg/hr)
DZB/ZnSt	A	40	793k	2.6	2.0	2.6
DZB/ZnSt	B	40	727k	2.5	2.0	3.0
DZB/ZnSt	D	40	655k	2.4	3.8	3.1

#### EXAMPLES 4-6: FARREL CONTINUOUS MIXER PHA COMPOUNDING

A Farrel CP250 continuous mixer/extruder was used for industrial scale compounding of BIOPOL pellets. Powder blends were obtained by adding the BN nucleant and the plasticizer to the powder contained in a 400 kg capacity blade blender in continuous rotation. The mixing chamber was fitted with a no.7 low shear rotor. The single screw extruder was fitted with a 100 mm screw and a 20 holes die. The strands were cooled in a 5 meters water bath containing water maintained at 55°C by circulating the water through a thermoregulator. Table 5 summarizes the conditions used to compound different pellets described in Examples 4-6.

TABLE 5: Continuous Mixer PHA Compounding

Example	4	5	6	6
<b>MIXER:</b>				
Feed rate (kg/hr)	200	200	200	200
Rotor speed (rpm)	500	400	350	300
Chamber temp.	210	200	190	190
Melt temp.	173	164	159	156
Orifice % open:	56	83	83	83
<b>EXTRUDER:</b>				
Screw speed (rpm)	65	60	60	60
Rear barrel temp.	140	140	140	140
Forward barrel temp.	160	160	160	160
Adapter temp.	190	180	180	180

Die plate temp.	190	180	180	180
Head pressure (bar)	71	102	104	112
Melt temp.	214	205	200	200
5    PELLETS:				
MFI(g/10 min.-170°C/5kg)	8	6	5	4.5
Mw	525 k	556 k	576 k	591 k
Mn	242 k	245 k	234 k	219 k
Mw/Mn	2.2	2.3	2.5	2.7
10				
All temperatures in degrees Celsius				

## EXAMPLE 4

A blend based on 100 phr BIOPOL powder (Mw=895k), 1 phr BN and 10 phr  
 15    ATC plasticizer fed into the FARREL CP 250 continuous mixer/extruder at a output rate  
 of 200 kg/Hr. The mixer and extruder conditions were as summarized in Table 5. A melt  
 temperature of 214° C and a head pressure of 71 bar were measured at the head of the  
 extruder. The pellets obtained had a Mw of 525k and a MFI of 8 g/10 min. (170° C/5kg)

## EXAMPLE 5

20    A blend based on 100 phr BIOPOL powder (Mw=895k), 1 phr BN and 10 phr ATC  
 plasticizer fed into the FARREL CP 250 continuous mixer/extruder at a output rate of 200  
 kg/hr. The mixer and extruder conditions were as summarized in Table 5. The rotor speed  
 was reduced to 400 rpm compared to Example 1 and the mixer chamber and extruder  
 adapter/ die temperatures were reduced by 10° C. A melt temperature of 214° C and a  
 25    head pressure of 71 bar were measured at the head of the extruder. The pellets obtained  
 had a Mw of 556k and a MFI of 6 g/10 min. (170° C/ 5 kg)

## EXAMPLE 6

Blends were compounded as in Example 5, however the rotor speeds were 350 and  
 300 rpm respectively. The pellets obtained for the blend having a rotor speed of 350rpm  
 30    had a Mw of 576k and an MFI of 5 g/10 min while the pellets obtained with a rotor speed  
 of 300 rpm had a Mw of 591k and an MFI of 4.5g/10min. (170° C/ 5 kg)

EXAMPLES 7-12:    EFFECT OF MOLECULAR WEIGHT ON THE PROCESSING  
 AND DRAWING OF BIOPOL FILMS



## EXAMPLE 7

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w = 390k$ , containing 8 mol% HV, 1 phr of Boron Nitride (BN) nucleant and 10 phr of Acetyltributylcitrate (ATC) plasticizer. The plasticized pellets were extruded through a 20mm single screw extruder fitted with a 25mm circular die using a temperature profile from 155 to 170° C and a screw speed of 20 rpm. The extruded tubular preform, which was cooled and blown with air to a 12 mm diameter bubble, showed instability, preventing bubble blowing to a larger diameter. The tubular film, collapsed between nip rolls, could not be drawn above a draw ratio of 3 without breaking.

## EXAMPLE 8

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w = 456k$ , containing 8 mol% HV, 1 phr of BN nucleant and 10 phr of ATC plasticizer. The plasticized pellets were extruded through a 20mm single screw extruder fitted with a 25mm circular die using a temperature profile from 155 to 170° C and a screw speed of 20 rpm. The extruded tubular preform, which was cooled and blown with air to a 25 mm diameter bubble, showed instability, preventing bubble blowing to a larger diameter. The tubular film, collapsed between nip rolls, could not be drawn above a draw ratio of 5.4 without breaking. At a draw ratio of 5.4, the orientation process was discontinuous.

## EXAMPLE 9

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w = 525k$ , containing 8 mol% HV, 1 phr of BN nucleant and 10 phr of ATC plasticizer. The plasticized pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 165° C. At a screw speed of 26 rpm, the extruded tubular preform, which was cooled and blown with air to a 25 mm diameter bubble, produced after collapsing between two nip rolls a film with a thickness of 90-110 microns, characterized by a tensile strength at break of 27 MPa and an elongation at break of 8-12%. The collapsed tubular film could be stretched in the machine direction in a continuous process up to a drawing ratio of about 5.8. 35-40 micron thick oriented film was obtained which was characterized by a tensile strength at break of 85 MPa and an elongation at break of 80-100%.

## EXAMPLE 10

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight Mw=625 k, containing 8 mol% HV, 1 phr of BN nucleant and 10 phr of ATC plasticizer. The plasticized pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 160 to 180° C. At a screw speed of 25 rpm, the extruded tubular preform, which was cooled and blown with air to a stable 25 mm diameter bubble, produced after collapsing between two nip rolls a film with a thickness of 110-140 microns, characterized by a tensile strength at break of 27 MPa and an elongation at break of 13-17 %. The collapsed tubular film could be stretched in the machine direction up to a drawing ratio of 5.8 in a continuous process. 50 micron thick oriented film was obtained which was characterized by a tensile strength at break of 101-138 MPa and an elongation at break of 75-85%.

## EXAMPLE 11

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight Mw=700k, containing 8 mol% HV, 1 phr BN nucleant system and 10 phr of ATC plasticizer. The plasticized PHA pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 160 to 180° C. At a screw speed of 20 rpm, the stiff extruded tubular preform could not be blown above a stable 20 mm diameter bubble, which produced after collapsing between two nip rolls a film with a thickness of 180-240 microns, characterized by a tensile strength at break of 27 MPa and an elongation at break of 14-30 %. The collapsed tubular film could be stretched in the machine direction up to a drawing ratio of 6 in a continuous process. 50 micron thick oriented film was obtained which was characterized by a tensile strength at break of 120 MPa and an elongation at break of 70-80%.

## EXAMPLE 12

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight Mw=796k, containing 8 mol% HV, 1 phr BN nucleant system and 10 phr of ATC plasticizer. The plasticized PHA pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 165 to 185° C. At a screw speed of 20 rpm, the stiff extruded tubular preform could not be blown above a

stable 18 mm diameter bubble, which produced after collapsing between two nip rolls a film with a thickness of 160-200 microns, characterized by a tensile strength at break of 27 MPa and an elongation at break of 17-45 %. The collapsed tubular film could be stretched in the machine direction up to a drawing ratio of 5.8 in a continuous process. 60 micron thick oriented film was obtained which was characterized by a tensile strength at break of 136 MPa and an elongation at break of 80-95 %.

The results of Examples 7-12 are summarized in Table 6 below.

TABLE 6: Effect of Molecular Weight on the Processing and Drawability of PHA films

Ex.	MW	%Elongation at break oriented/unoriented	Tensile Strength at break, MPa oriented/unoriented
-----	----	--	--

7	390 k	Unstable bubble - No continuous orientation	
8	456 k	Unstable bubble- No continuous orientation	
9	525 k	80-100/8-12	85/27
10	625 k	75-85/13-17	101-138/27
11	700 k	70-80/14-30	120/27
12	796 k	80-95/17-45	136/27

All formulations contained 1 phr boron nitride (BN) nucleant and 10 phr acetyltributylcitrate (ATC) plasticizer

Examples 7-12 demonstrate that it is necessary to use PHA pellets having a sufficiently high Mw in order to achieve a stable process by which unsupported film can be blown and oriented.

#### EXAMPLES 13-16: EFFECT OF PLASTICIZER AND NUCLEANT SYSTEM ON THE PROCESSING AND DRAWABILITY OF BIOPOL FILMS

##### EXAMPLE 13

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight Mw =500k, containing 8 mole % HV and 1 phr of BN nucleant. The unplasticized PHA pellets, compounded first by extrusion of PHBV powder blend with the additives, were extruded through a 20mm single screw extruder fitted with a 25mm circular die using a temperature profile from 165 to 175°C and a screw speed of 16rpm. The extruded tubular preform, which was cooled and blown with air to a 12 mm diameter stiff bubble, showed instability, preventing bubble blowing to a larger diameter. The tubular film, collapsed

between nip rolls, had a thickness of 80 microns, an elongation at break of 6% and a tensile strength of 22%. This film could not be drawn above a draw ratio of about 3 without breaking. The oriented film obtained in a discontinuous process had a thickness of 35 microns, an elongation at break of 65% and a tensile strength at break of 62 MPa.

5

## EXAMPLE 14

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w = 500k$ , containing 8 mole % HV, 1 phr of BN nucleant and 3 phr ATC plasticizer. The plasticized PHA pellets, compounded first by extrusion of PHBV powder blend with the additives, were extruded through a 20mm single screw extruder fitted with a 25mm  
10 circular die using a temperature profile from 155 to 170°C and a screw speed of 20 rpm. The extruded tubular preform was cooled and blown with air to a 25 mm diameter stiff bubble. The tubular film collapsed between nip rolls had a thickness of 80 microns, an elongation at break of 6% and a tensile strength of 22%. This film could not be drawn above a draw ratio of 3 without breaking. The oriented film obtained in a discontinuous  
15 process had a thickness of 35 microns, an elongation at break of 66% and a tensile strength at break of 61 MPa.

## EXAMPLE 15

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w = 500k$ , containing 8 mole % HV, 1 phr of BN nucleant and 6 phr ATC plasticizer.  
20 The plasticized PHA pellets, compounded first by extrusion of PHBV powder blend with the additives, were extruded through a 20mm single screw extruder fitted with a 25mm circular die using a temperature profile from 155 to 165°C and a screw speed of 25 rpm. The extruded tubular preform was cooled and blown with air to a 35 mm diameter bubble. The tubular film, collapsed between nip rolls, had a thickness of 100 microns, an  
25 elongation at break of 9% and a tensile strength of 23%. This film could not be drawn above a draw ratio of 3 without breaking. The oriented film obtained in a discontinuous process had a thickness of 50 microns, an elongation at break of 72% and a tensile strength at break of 58 MPa.

## EXAMPLE 16

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w=525k$  and  $M_n=242k$ , containing 8 mole % HV, 1 phr of BN nucleant and 10 phr of ATC plasticizer. The plasticized PHA pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 165°C. At a screw speed of 26 rpm, the extruded tubular preform, which was cooled and blown with air to a stable 30 mm diameter bubble produced after collapsing between two nip rolls a film with a thickness of 110 microns, characterized by a tensile strength at break of 17 MPa and an elongation at break of 8%. The collapsed tubular film could be stretched in the machine direction in a continuous process with a drawing ratio of about 5. The 35 micron thick oriented film obtained was characterized by a tensile strength at break of 85 MPa and an elongation at break of 80%. The PHBV in the film was found to have  $M_w = 451k$  and  $M_n = 211k$  which corresponds to a loss in  $M_w$  of 14% and a loss in  $M_n$  of 12.7%.

The results of Examples 13-16 are summarized in the following Table:

TABLE 7:

Ex.	MW	ATC level phr	%Elongation at break oriented/unoriented	Tensile Strength at break,MPa oriented/unoriented
13	500k	0	65/6	62/22
14	500k	3	66/6	61/22
15	500k	6	72/9	58/23
16	500k	10	80/8	85/17

All formulations contained 1 phr BN nucleant

## EXAMPLE 17

In this example, the PHA in the pellet was a PHBV copolymer of molecular weight  $M_w=508k$  and  $M_n=215k$ , containing 8 mol% HV, 0.1 phr Cyclohexylphosphonic acid (DZB) / 0.4 phr Zinc Stearate (ZnSt) nucleant system and 10 phr of ATC plasticizer. The plasticized PHA pellets were extruded through a 20mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 165°C. At a screw speed of

13 rpm, the extruded tubular preform, which was cooled and blown with air to a stable 25 mm diameter bubble produced after collapsing between two nip rolls a stiff semi-transparent film with a thickness of 90 microns, characterized by a tensile strength at break of 20 MPa and an elongation at break of 13%. The collapsed tubular film could be stretched in the machine direction up to a drawing ratio of about 6 in a continuous process. The 40 micron thick clear oriented film obtained was characterized by a tensile strength at break of 90 MPa and an elongation at break of 75%. The PHBV in the film was found to have  $M_w = 493k$  and  $M_n = 211k$  corresponding to a loss in  $M_w$  of 2.9% and a loss in  $M_n$  of 1.9%.

Table 8:

Ex	MW (pellet)	Nucleant	%Elongation at break (oriented/unoriented)	Tensile Strength at break, MPa (oriented/unoriented)
16	525k	BN	80/8	58/17
17	508k	DZB/ZnSt	75/13	90/20

EXAMPLES 18-21: THERMOSTABILIZATION OF PHA: Based upon the results of Example 17 where in the presence of DZB/ZnSt very little PHA  $M_w$  loss was observed in the film when compared to the  $M_w$  of the pellets used to produce the film, the following experiments were carried out:

## EXAMPLE 18

PHBV pellets compounded from formulations based on BIOPOL powder of  $M_w=895k$ , 10 phr ATC plasticizer, and respectively 1 phr BN or a combination of 0.1 phr cyclohexyl phosphonic acid (DZB) and 0.4 phr zinc stearate (ZnSt). The two powder blends prepared in a Pappenmeier high speed blender were fed in a 25 mm Betol single screw extruder ( $L/D=20$ ) fitted with a 4mm diameter single strand circular die using barrel temperature profile of 140 to 160°C and a screw speed of 60 rpm. The extruded strand was cooled and crystallized in a 5 meter long water bath held at 50-60°C using a thermoregulator and then cut into cylindrical pellets with a 3-4mm diameter and 3-5mm

length in a pelletizer. The PHA in the pellets containing either BN or DZB/ZnSt had Mw = 706k and 757k respectively.

#### EXAMPLE 19

PHBV pellets compounded from formulations based on BIOPOL powder of  
5 Mw=895k, 10 phr ATC plasticizer, and respectively 1 phr BN or a combination of 0.1 phr  
cyclohexyl phosphonic acid (DZB) and 0.4 phr zinc stearate (ZnSt). The two powder  
blends prepared in a Pappenmeier high speed blender were fed in a 25 mm Betol single  
screw extruder (L/D=20) fitted with a 4mm diameter single strand circular die using barrel  
temperature profile of 150 to 180°C and a screw speed of 40 rpm. The extruded strand  
10 was cooled and crystallized in a 5 meter long water bath held at 50-60°C using a  
thermoregulator and then cut into cylindrical pellets with a 3-4mm diameter and 3-5mm  
length in a pelletizer. The PHA in the pellets containing either BN or DZB/ZnSt had Mw  
= 625k and 655k respectively.

#### EXAMPLE 20

15 PHBV pellets compounded from formulations based on BIOPOL powder of  
Mw=679k, 10 phr ATC plasticizer, and respectively 1 phr BN or a combination of 0.1 phr  
cyclohexyl phosphonic acid (DZB) and 0.4 phr zinc stearate (ZnSt). The two powder  
blends prepared in a Pappenmeier high speed blender were fed in a 25 mm Betol single  
screw extruder (L/D=20) fitted with a 4mm diameter single strand circular die using barrel  
20 temperature profile of 140 to 170°C and a screw speed of 40 rpm. The extruded strand  
was cooled and crystallized in a 5 meter long water bath held at 50-60°C using a  
thermoregulator and then cut into cylindrical pellets with a 3-4mm diameter and 3-5mm  
length in a pelletizer. The PHA in the pellets containing either BN or DZB/ZnSt had Mw  
= 571k and 618k respectively.

25 The results of Examples 18-20 are summarized in Table 9 below and demonstrate  
that DZB/ZnSt can serve as a thermal stabilizer during pellet production.

TABLE 9

Nucleant System	Mw of PHVB Powder	Mw of PHBV Pellets	%Reduction
BN	895k	706k	21.1
DZB/ZnSt	895k	757k	15.4
BN	895k	625k	30.2
DZB/ZnSt	895k	655k	26.8
BN	679k	571k	15.9
DZB/ZnSt	679k	618k	9.0

5

10

15

## EXAMPLE 21

PHBV films were obtained by extrusion blowing using a 20mm Brabender single screw extruder (L/D=20) fitted with a 25mm circular die of the spider type and with a Brabender single screw force feeder to handle powders, using a barrel temperature profile of 155-165°C and a screw speed of 25 rpm. PHA pellets were based on PHBV copolymers of Mw= 525k and 508k containing 10 phr ATC plasticizer, and respectively 1 phr BN nucleant or 0.1 phr DZB/0.4 phr ZnSt. The films obtained by blowing a bubble of 25mm diameter and collapsing it between two nip rolls had a thickness after separation of the two layers of about 110 microns and had MW= 451k and 493k respectively. The results are summarized in Table 10 below, demonstrating that the presence of DZB/ZnSt in PHA pellets can serve as a thermal stabilizer during film extrusion/production.

25

TABLE 10

Nucleant System	Mw of PHVB in Pellets	Mw of PHBV in Film	%Reduction
BN	525k	451k	14.1
DZB/ZnSt	508k	493k	3.0

30

35

## EXAMPLE 22

Compositions were prepared by mixing PHBV copolymer (10% HV) (500 g) with 1 phr boron nitride (as nucleant) and 20 phr of plasticizer. The mixture was extruded in a



Betol 2520 extruder under these conditions: Zone 1 = 130°C; Zone 2 = 140°C; Zone 3 = 150°C; Die = 150°C; Screw Speed = 100 rpm. The extrudate, a single 4mm lace, was crystallized at 50-60°C in a water bath, dried in a current of air and cut into granules. The granules were then injection molded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mold, then allowed to cool at ambient temperature. Injection molding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 130°C; Mold heater temperature = 74-77°C; Mold temperature = 60°C; Pressure hold on time = 12 sec; Cooling time = 30 sec; Injection pressure 45 bar; Screw speed = 250 rpm.

Tensile testing was carried out using an Instron 1122 fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were measured after 30 days for elongation at break. The results are presented in Table 11 in percentage elongation to break (E%) relative to the starting gauge length of 40mm.

#### Glass transition temperature ( $T_g$ measurements)

The compositions were prepared by dispersing the plasticizer (20 phr) onto 10g of PHBV copolymer (10% HV). The plasticizer was dissolved in 20-25ml methanol (or chloroform if immiscible with methanol) and the polymer powder fully wetted. The solvent was allowed to evaporate off at room temperature for 3-4 hours before the blend was finally dried at 60°C for 30 minutes.

The  $T_g$  measurement were carried out by differential scanning calorimetry (DSC) analysis using a Perkin Elmer DSC7 under a nitrogen atmosphere. 10mg samples were used in the following temperature regime : melt sample at 200°C for 2 minutes, cool rapidly to -80°C and hold at this temperature until the system has equilibrated. Heat at 20°C min<sup>-1</sup> from -80°C to 50°C. The  $T_g$  was reported as the point of inflection (in the trace) for the second heating step.

TABLE 11

Plasticizer	T <sub>g</sub> /°C	E (%)
No plasticizer	0	8.5
poly(ethylene glycol) PEG 200)	-19.5	10
poly(ethylene glycol) (PEG 300)	-20.5	11.75
poly(propylene glycol) (PPG 1000)	-10.19	12.75
ditridecyl phthalate	-10.92	12.75
poly(oxyethylene) (4)lauryl ether (Brij 30)	-9.3	13.75
poly(oxyethylene) (20)sorbitan monolaurate (Tween 20)	-16.6	14
di-isoundecylphthalate (Jayflex DIUP)	-8.38	14.5
polycaprolactone triol (PCL (Mw 300)	-8.3	15.75
poly(propylene glycol) (PPG 425)	-23.13	16.75
di-isononylphthalate (Jayflex DINP)	-12.77	16.75
di-isoheptylphthalate (Jayflex 77 DIHP)	-19.42	20
poly(propylene glycol) (PPG 725)	-14.2	21.5
di-iso-octylphthalate (Jayflex DIOP)	-15.84	22
di-isodecylphthalate (Jayflex DIDP)	-10.06	22.5
epoxidised soya bean oil (Reoplast 39)	-9.5	34.25

The plasticizers used in this example are available from commercial suppliers (BDH, Aldrich Chemicals, Exxon Chemicals, and Ciba Geigy).

5

## EXAMPLE 23

Compositions were prepared by mixing PHBV copolymer (11% HV) (500 g) with 1 phr boron nitride (as nucleant) and 100g (20 phr) of plasticizer. The mixture was extruded in a Betol 2520 extruder under the following conditions: Zone 1 = 115°C; Zone 2 = 133°C; Zone 3 = 153°C; Die = 158°C, Screw Speed = 100 rpm. The extrudate, a single 4mm lace, was crystallized at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules. The granules were then injection molded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part

10

measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mold. Injection molding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 134°C; Mold heater temperature 74-77°C; Mold temperature = 60°C; Pressure hold on time = 12 sec; cooling time = 12 sec; injection pressure = 45 bar; Screw speed = 250 rpm.

Tensile testing was carried out using an Instron 1122 fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were measured after 90 days for elongation at break. The results are presented in Table 12 as percentage elongation to break relative to the starting gauge length of 40 mm. The T<sub>g</sub> tests of this example were carried out on samples taken from the extruded lace. The DSC analysis was conducted as in Example 22 except for the following conditions: sample size = 7-10 mg; sample cooled rapidly to -50°C at 100°C min<sup>-1</sup>; allowed to equilibrate at -50°C; heated at 20°C min<sup>-1</sup> to 205°C.

The plasticizers used in this example are available from commercial suppliers (Unichema International, Akzo Chemie, FMC Corporation, C.P. Hall, ICI, Kemira Polymers).

TABLE 12

Plasticizer	T <sub>g</sub> /°C	E(%)
No plasticizer	0.8	13.5
D-A Sebacate	-8.7	16.5
glycerol diacetate (Estol 1582)	-12.9	19.5
toluene sulphonamide (Ketjenflex 3)	-8.6	21.8
toluene sulphonamide (Ketjenflex 7)	-10.2	24
di-2-ethylhexyl adipate (Reomol DOA)	-10.7	26.5
butyl acetyl ricinoleate (BAR)	-8.5	28.3
di-isobutylphthalate (Reomol DiBP)	-16	28.5
diester ether alkyl (Plasthall 7050)	-26.3	29.3
toluene sulphonamide (Ketjenflex 8)	-7.8	29.3
triethylene glycol diacetate (Estol 1593)	-28	32
triethylene glycol caprylate (Plasthall 4141)	-24	34
alkyl aryl phosphate (Ketjenflex 141)	-17.8	34.5

toluene sulphonamide (Ketjenflex 15)	-7.4	38
chlorinated paraffin (Cereclor 56L)	-7.2	41.5
polyester (Reoplex 346)	-16.4	42.3
di-isodecylphthalate (Reomol DiDP)	-6.6	43.8
adipic polyester (Plasthall 643)	-11.4	45
butyl benzyl phthalate (Ketjenflex 160)	-13.8	45.3
chlorinated paraffin (Cerechlor 552)	-11.8	51.5
Wolflex-But	-9.8	52.8
glutaric polyester (Plasthall 550)	-7.8	52.8
polyester (Reoplex 1102)	-13.5	53.5
polymeric ester (Diorex 570)	-14	54.3
polymeric ester (Diolpate OL1696)	-15	54.8
tri-isopropyl phenyl phosphate (Reofos 95)	-9.2	55.3
phosphate ester (Reomol 249)	-17.3	60.8

## EXAMPLE 24

Compositions were prepared by mixing PHBV copolymer (6.6% HV, Mw of 680,000) with 1 phr boron nitride (as nucleant) and 20 phr of plasticizer. The mixture was  
5 blended for 10 minutes then extruded in a Betol 2520 extruder under the following conditions:

- Zone 1 = non-plasticized 140°C; plasticized 130°C;  
Zone 2 = non-plasticized 150°C; plasticized 140°;  
Zone 3 = non-plasticized 160°C; plasticized 140°C;  
10 Die = non-plasticized 160°C; plasticized 150°C;

The extrudate, a single 4mm lace, was crystallized at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules. The granules were then injection molded (Boy 305) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out  
15 of the mold.

Injection molding conditions were:

Zones 1 to 3 temperature = as for the extrusion process;

Injection time = 16 seconds;

Nozzle temperature = 150°C;

Mold heater temperature = 60-70°C;

5 Mold temperature = 60°C;

Pressure hold on time = 16 sec;

Cooling time = 16 sec;

Screw speed = 240 rpm.

Tensile testing was carried out using an Instron 4501 instrument system. The jaw  
 10 separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were  
 measured after 30 days for elongation at break. The results are presented in Table 13 as  
 percentage elongation to break relative to a starting gauge length of 40mm. The T<sub>g</sub> tests of  
 this example were carried out on samples from the injection molded test pieces. The DSC  
 analysis was conducted as in Example 22 except for the following conditions: sample size  
 15 = 7-10 mg; sample cooled rapidly to -80°C at 100°C min<sup>-1</sup>; allowed to equilibrate at -  
 80°C; heated at 20°C min<sup>-1</sup> to 200°C. The results are presented in Table 13 as percentage  
 elongation to break relative to a starting gauge length of 40mm.

Impact testing was carried out on a notched impact test piece of 11.8mm x 1.3mm  
 x 4mm using a Zwick Izod impact tester at 28°C. The results are presented in Table 3.

20 Where a T<sub>g</sub> is available for the material this is placed alongside the result in the Table.

TABLE 13

Plasticizer	%E	T <sub>g</sub>	Plasticizer	IZOD	T <sub>g</sub>
None	15.4		None	70.8	
1	15.4		5	71	
2	18.5		53	98.8	
3	16.7		44	104	
4	17.0		4	105	
5	17.4		18	107.8	-8.3
6	17.7	-11.9	38	110	
7	18.9		41	110.3	1.39

8	18.9		17	111.3	
9	19.1	-13.5	26	111.8	
10	20.4		56	112	
11	20.5	-19.6	23	117	
12	21.3		15	125	
13	22	-12.7	50	125.3	
14	22.1	-18.6	1	127.1	
15	23.1		17	128	
16	23.3		64	129.8	-22.8
17	24.2		65	130.3	-10.5
18	24.6	-8.3	10	130.3	
19	24.7	-12.6	66	135	-7.5
20	25	-8.5	3	136.8	
21	25		32	138	
22	25		21	142.8	
23	25.2		60	144.8	
24	25.6	-4.2	48	149.8	-3.67
25	26.1	-3.8	52	152	
26	26.2		47	155.8	
27	26.8	-25.3	7	155.8	
28	27.8	-22.8	40	159	
29	29.4	-21.5	36	160.8	
30	29.6	-18.5	34	164.3	-6.5
31	29.6	-6.1	51	164.8	
32	30.2		63	166.3	-3.5
33	30.3	-17.9	49	166.8	-15.8
34	30.8	-6.5	58	166.8	
35	31.1		43	167.3	
36	31.3		16	167.8	
37	31.3	-18.3	6	169.4	-11.9
38	31.7		29	170.8	-21.5
39	33.3	-26.2	62	182.3	-6.6

40	34.2		33	183.3	-17.9
41	34.3	-1.4	56	185	
42	34.4	-22.0	13	186.6	-12.7
43	35.3	-10.8	45	187.3	-6.3
44	35.4		31	192.8	-6.1
45	36	-6.3	2	195.4	
46	36.4	-2.1	67	197.5	-3.1
47	38.5		19	197.8	-12.6
48	38.6	-3.7	61	197.8	
49	39	-15.8	59	198.8	-13
50	40.5		57	200.8	-4.2
51	40.6		68	201.8	-25.3
52	42.9		14	202.8	-18.6
53	47.6		35	204.8	
54	48.4	-14.5	25	215.8	-3.8
55	48.4	-1.2	9	220.8	-13.5
56	48.6		37	227.3	-18.3
57	55.7	-4.2	38	227.8	
58	59.3		42	228.3	-22
59	60.7	-13.0	39	231.8	-26.2
60	68.9		11	235.6	-19.6
61	82.3		55	241	-1.2
62	96.6	-6.56	20	243.3	-8.5
63	162.7	-3.49	30	251.8	-18.5
			69	257.8	-1.5
			54	271.3	-14.5
			22	273.8	
			46	301.3	-2.1
			12	265.8	

## Key

- 1 1,4-butane diol adipic acid (S102250) available from Occidental Chemical

- 2 1,4-butane diol adipic acid (S102250) (35phr)  
3 polyethylene glycol 2000 available from Aldrich Chemical  
4 polycaprolactone (Tone 301) available from Union Carbide  
5 polyethylene glycol 6000 available from Aldrich Chemical  
5 6 Triton X100 (polyethoxyethanol) available from Aldrich Chemical  
7 1,4-butane diol adipic acid (S1063210) available from Occidental Chemical  
8 neopentylglycol-adipic acid-caprolactone (S1063210) available from Occidental  
Chemical  
9 triethylcitrate (Citroflex 2) available from Morflex Inc.  
10 10 polyester adipate (MW = 2000) (Plasthall P643) available from C.P. Hall  
11 Morton TP95 (polyether) available from Morton Thiokol Inc.  
12 di-isononyladipate (Jayflex DINA2) available from Exxon Chemical  
13 Reomol 249 (phosphate ester) available from FMC Corporation  
14 Monoplex 573 (epoxidised octyl tallate) available from C.P. Hall  
15 15 PEG 600 monolaurate (Plasthall CPH43N) available from C.P. Hall  
16 Epoxidised soyabean oil (Plasthall ESO) available from C.P. Hall  
17 PEG 200 Monolaurate (Plasthall CPH27N) available from C.P. Hall  
18 Epoxidised soya bean oil (Paraplex G60) available from C.P. Hall  
19 acetyl tri-n-butyl citrate (Citroflex A4) available from Morflex Inc.  
20 20 acetyl triethyl citrate (Citroflex A2) available from Morflex Inc.  
21 polyester sebecate (Plasthall P1070) available from C.P. Hall  
22 neopentylglycol-adipic acid-caprolactone (S1063210) (35phr) available from  
Occidental Chemical  
23 F1040250 trifunctional polyester adipates available from Occidental Chemical  
25 24 polypropylene glycol adipate (low MW) (Lankroflex PPL) available from  
Harcros Chemicals  
25 di isooctylazelate (Reomol DiOZ) available from FMC Corporation  
26 polyester adipate (MW = 1200) (Plasthall P650) available from C.P. Hall  
27 Butyl carbitol ether/ester (Reomol BCF) available from FMC Corporation  
30 28 epoxidised linseed oil (Lankroflex L) available from Harcros Chemicals



- 29 epoxidised ester of fatty acid (Lankroflex ED6) available from Harcros Chemicals
- 30 tri-n-butylcitrate (Citroflex 4) available from Morflex Inc.
- 31 epoxidised soyabean oil (Paraplex G62) available from C.P. Hall
- 5 32 polyoxyethylene laurate (Plasthall CPH 376N) available from C.P. Hall
- 33 Morton TP759 available from Morton Thiokol
- 34 dioctyladipate (Jayflex DOA2) available from Exxon Chemical
- 35 polyester glutarate (Plasthall P7092) available from C.P. Hall
- 36 polyester adipate (Diolpate 917) available from Kemira Chemical
- 10 37 butyl carbitol ether/ester (Reomol BCD) available from FMC Corporation
- 38 octylphenyl substituted PEG (Igepal CA520)
- 39 Morton TP90B available from Morton Thiokol
- 40 trifunctional polyester adipates (F1040250) (35phr) available from Occidental Chemical
- 15 41 epoxidised soya bean oil (Lankroflex GE) available from Harcros Chemical
- 42 acetyltributylcitrate (Estaflex\*) available from Akzo Chemie
- 43 acetyltrimethylcitrate available from Morflex Inc.
- 44 PEG 600 monooleate (Plasthall CPH41N) available from C.P. Hall
- 45 butyl-tri-n-hexyl citrate (Citroflex B6) available from Morflex Inc.
- 20 46 di-isodecyladipate (Jayflex DIDA2) available from Exxon Chemical
- 47 polyester adipate (Diolpate 214) available from Kemira Polymers
- 48 epoxidised soya bean oil (Reoplas 39) available from Ciba Geigy
- 49 di-n-butyl sebecate (Reomol DBS) available from Ciba Geigy
- 50 polyester adipate (MW=4200) (Diolpate 214) available from Kernira Polymers
- 25 51 epoxidised glycol oleate (Monoplex S75) available from C.P. Hall
- 52 PEG 400 Monolaurate (Plasthall CPH30N) available from C.P. Hall
- 53 Castor oil available from Aldrich Chemical
- 54 Estaflex\*/epoxidised soyabean oil (Reoplas 39) (50/50) available from Akzo Chemie/Ciba Geigy
- 30 55 polyester glutarate (Paraplex P550) available from C.P. Hall
- 56 S1069285 (35phr) available from Occidental Chemical

- 57 PPG phthalate/adipate blend (Lankroflex 828) available from Harcros Chemical  
58 polyester adipate (Paraplex G59) available from C.P. Hall  
59 tri-isopropyl phenyl phosphate (Reofos 95) available from FMC Corporation  
60 polypropylene adipate (Diolpaté PPA350) available from Kemira Polymers  
5 61 polyester glutarate (Plasthall P7035) available from C.P. Hall  
62 PEG mono (1,1,3,3-tetramethylbutyl-phenyl ether (Igepal CA210) available from Aldrich Chemical  
63 polypropyleneglycol adipate high MW (Lankroflex PPA3) available from Harcros Chemical  
10 64 PEG 200 monooleate (Plasthall CPH27N) available from C.P. Hall  
65 polyoxyethylene sorbitanmonolaurate (Tween 80) available from Aldrich Chemical  
66 trimethylcitrate available from Morflex Inc.  
67 polyester glutarate (Plasthall P7046) available from C.P. Hall  
15 68 butyl carbitol ether/ester (Reomol BCF) available from FMC Corporation  
69 mixed polyester (Reomol MD) (ester of mixed adipic, glutaric and succinic acids with isodecanol) available from FMC Corporation

#### EXAMPLE 25

The PHA was a plasticized PHBV copolymer of molecular weight  $M_w=661K$ ,  
20 containing 8 mole % HV, 1 phr Boron nitride nucleant and 10 phr Acetyl tri n-butyl citrate plasticizer. The plasticized granules, compounded first by extrusion of the PHBV powder blend with the additives mixed in a Pappenmeier high speed mixer, were extruded through a 20 mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 175 dC and a screw speed of 20 mm. The extruded tubular preform, which  
25 was cooled and blown with air to a 20 mm diameter stable bubble, was collapsed between the first nip rolls of the blowing tower to produce a film with a thickness of 150-170 micron, characterized by a tensile strength of 26-30 MPa and an elongation at break of 16-28%. The collapsed tubular film could be continuously stretched after the first nip rolls by increasing the speed of the second nip rolls, keeping the first nip rolls speed constant at 2.5  
30 m/min up to a draw ratio of 5. The 50 micron oriented film obtained was characterized by a tensile strength of 85-120 MPa and an elongation at break of 85-114%.

## EXAMPLE 26

The PHA was a plasticized PHBV copolymer of molecular weight  $M_w=601K$ , containing 8 mole % HV, 1 phr Boron nitride nucleant and 10 phr Santicizer 409A polyester plasticizer. The plasticized granules, compounded first by extrusion of the PHBV powder blend with the additives mixed in a Pappenmeier high speed mixer, were extruded through a 20 mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 175 dC and a screw speed of 20 mm. The extruded tubular preform, which was cooled and blown with air to a 20 mm diameter stable bubble, was collapsed between the first nip rolls of the blowing tower to produce a film with a thickness of 80-140 micron, characterized by a tensile strength of 26-32 MPa and an elongation at break of 66-200%. The collapsed tubular film could be easily stretched in a continuous process, after the first nip rolls by increasing the speed of the second nip rolls, keeping the first nip rolls speed constant at 2.5 m/min up to a draw ratio of 5.6. The 40-70 micron oriented film obtained was characterized by a tensile strength of 110-154 MPa and an elongation at break of 75-117%.

## EXAMPLE 27

The PHA was a plasticized PHBV copolymer of molecular weight  $M_w=583K$ , containing 8 mole % HV, 1 phr Boron nitride nucleant and 10 phr Santicizer 433 polyester plasticizer. The plasticized granules, compounded first by extrusion of the PHBV powder blend with the additives mixed in a Pappenmeier high speed mixer, were extruded through a 20 mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 175 dC and a screw speed of 20 mm. The extruded tubular preform, which was cooled and blown with air to a 20 mm diameter stable bubble, was collapsed between the first nip rolls of the blowing tower to produce a film with a thickness of 120-140 micron, characterized by a tensile strength of 26-27 MPa and an elongation at break of 50-160%. The collapsed tubular film could be easily stretched in a continuous process, after the first nip rolls by increasing the speed of the second nip rolls, keeping the first nip rolls speed constant at 2.5 m/min up to a draw ratio of 5.6. The 40-80 micron oriented film obtained was characterized by a tensile strength of 104-138 MPa and an elongation at break of 75-125%.

## EXAMPLE 28

The PHA was a plasticized PHBV copolymer of molecular weight  $M_w=568K$ , containing 8 mole % HV, 1 phr Boron nitride nucleant and 10 phr Santicizer 421 polyester plasticizer. The plasticized granules, compounded first by extrusion of the PHBV powder  
 5 blend with the additives mixed in a Pappenmeier high speed mixer, were extruded through a 20 mm single screw extruder fitted with a 25 mm circular die using a temperature profile from 155 to 175 dC and a screw speed of 20 mm. The extruded tubular preform, which was cooled and blown with air to a 20 mm diameter stable bubble, was collapsed between the first nip rolls of the blowing tower to produce a film with a thickness of 110-160  
 10 micron, characterized by a tensile strength of 25-32 MPa and an elongation at break of 18-33%. The collapsed tubular film could easily be stretched in a continuous process, after the first nip rolls by increasing the speed of the second nip rolls, keeping the first nip rolls speed constant at 2.5 m/min up to a draw ratio of 5.6. The 40-80 micron oriented film obtained was characterized by a tensile strength of 103-129 MPa and an elongation at  
 15 break of 78-112%.

TABLE 14

Summarized results of examples 25-28

Plasticizer	Mw K	% Elongation at break oriented/unoriented	Tensile strength at break, MPa oriented/unoriented
10 phr ATC	661	85-114/16-28	85-120/26-30
10 phr S409A	601	75-117/66-200	110-154/26-32
10 phr S433	583	75-125/50-160	104-138/26-27
10 phr S421	568	78-112/18-33	103-129/25-32

All of the compositions and methods disclosed and claimed herein can be made  
 20 and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. More

specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of

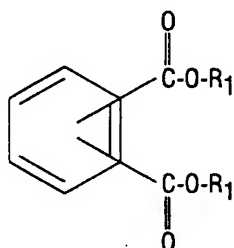
5 the invention as defined by the appended claims.

## CLAIMS

1. Polyester pellet composition comprising a polyhydroxyalkanoate (PHA) having a molecular weight of greater than about 470,000 and a plasticizing quantity of at least one  
5 plasticizer selected from the group consisting of:

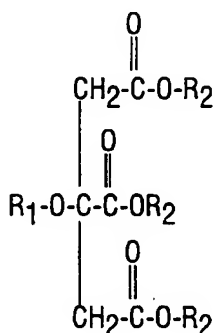
A. high boiling point esters selected from:

- 10 (i) phthalates and isophthalates of the formula:



where  $R_1$  is  $C_{1-20}$  alkyl, cycloalkyl or benzyl;

- 15 (ii) citrates of the formula:



- 20 where  $R_1$  is hydrogen or  $C_{1-10}$  alkyl, and  $R_2$  is  $C_{1-10}$  alkyl,  $C_{1-10}$  alkoxy or  $C_{1-10}$  alkoxyalkyl;

- (iii) adipates of the formula  $R_1-O-C(O)-(CH_2)_4-C(O)-OR_2$  where  $R_1$  and  $R_2$  which may be the same or different are  $C_{2-12}$  alkyl or  $C_{2-12}$  alkoxyalkyl;

- (iv) sebacates of the formula  $R_1-O-C(O)-(CH_2)_8-C(O)-O-R_1$  where  $R_1$  is  $C_{2-15}$  alkyl or  $C_{2-15}$  alkoxyalkyl;
- (v) azelates of the formula  $R_1-O-C(O)-(CH_2)_7-C(O)-R_1$  where  $R_1$  is  $C_{2-12}$  alkyl, benzyl, or  $C_{2-12}$  alkoxyalkyl;
- 5 B. alkyl ethers/esters of the formula  $R_2-(O-CH_2-CH_2)_n-O-R_1$  where  $R_1$  is alkyl or  $-C(O)-alkyl$ ,  $R_2$  is alkyl and  $n$  is 2 to 100; or where  $R_1$  is hydrogen and either:  $R_2$  is alkylphenyl where the alkyl is  $C_{2-12}$  alkyl, and  $n$  is 1 to 100; or  $R_2$  is  $CH_3-(CH_2)_{10}-C(O)-$  and  $n$  is 5, 10, or 15; or  $R_2$  is  $CH_3-(CH_2)_7CH=CH-(CH_2)_7-C(O)-$  and  $n$  is 5 or 15;
- 10 C. epoxy derivatives of the formula  $CH_3-(CH_2)_n-A-(CH_2)_n-R$  in which the A is an alkene containing one or more double bonds (i.e. unsaturated fatty acids),  $n$  is 1 to 25 and  $R$  is  $C_{2-15}$  alkyl; or epoxy derivatives of triglycerides containing one or more double bonds per fatty acid chain with chain lengths from  $C_6-26$ .
- 15 D. substituted fatty acids selected from palmitates, stearates, oleates, ricinoleates and laurates; and
- 20 E. polymeric esters of the formula  $-O-C(O)-R_1-C(O)-O-R_2-O-$  in which  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene, or  $R_2$  may be derived from a diol.
2. Polyester composition according to claim 1 wherein the polymeric ester is selected from glutaric polyesters having molecular weights from 2000 to 20,000, adipic polyesters having a molecular weight from 200 to 20,000, succinic polyesters, sebacic polyesters having a molecular weight from 4000 to 10,000, lactone copolymers of the formula  $[-(O-C(O)-R_1-C(O)-O-R_2-O)]_m-[(C(O)-R_3-O)]_n$  where  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene, or  $R_2$  may be derived from a diol, and  $R_3$  is  $-(CH_2)_5-$  (based on caprolactone),
- 30 polyesters of mixed adipic, glutaric and succinic acids, polycaprolactone triol.

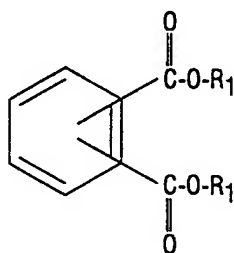
3. Polyester composition according to claim 1 wherein the polymeric ester is selected from poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,3-butylene glycol adipic acid) unterminated, poly(1,3-butylene glycol  
 5 adipic acid) unterminated, poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,3-butylene glycol adipic acid) terminated with mixed fatty  
 10 acids, poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,4-butylene glycol adipic acid), or poly(1,4-butylene glycol-co-ethylene glycol adipic acid).

15 4. A method of producing a shaped polymeric object comprising melting a composition comprising a polyhydroxyalkanoate (PHA) having a molecular weight of greater than about 470,000 and producing a shaped object therefrom by extrusion, molding, coating, spinning or calendaring operations, wherein the composition has a plasticizing quantity of at least one plasticizer selected from the group consisting:

20

A. high boiling point esters selected from:

(i) phthalates and isophthalates of the formula:



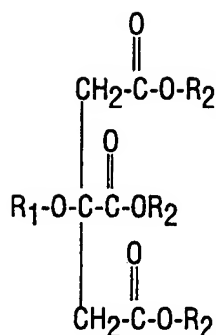
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where  $R_1$  is  $C_{1-20}$  alkyl, cycloalkyl or benzyl;

(ii) citrates of the formula:

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where  $\text{R}_1$  is hydrogen or  $\text{C}_{1-10}$  alkyl, and  $\text{R}_2$  is  $\text{C}_{1-10}$  alkyl,  $\text{C}_{1-10}$  alkoxy or  $\text{C}_{1-10}$  alkoxyalkyl;

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(iii) adipates of the formula  $\text{R}_1-\text{O}-\text{C}(\text{O})-(\text{CH}_2)_4-\text{C}(\text{O})-\text{O}-\text{R}_2$  where  $\text{R}_1$  and  $\text{R}_2$  which may be the same or different are  $\text{C}_{2-12}$  alkyl or  $\text{C}_{2-12}$  alkoxyalkyl;

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(iv) sebacates of the formula  $\text{R}_1-\text{O}-\text{C}(\text{O})-(\text{CH}_2)_8-\text{C}(\text{O})-\text{O}-\text{R}_1$  where  $\text{R}_1$  is  $\text{C}_{2-15}$  alkyl or  $\text{C}_{2-15}$  alkoxyalkyl;

(v) azelates of the formula  $\text{R}_1-\text{O}-\text{C}(\text{O})-(\text{CH}_2)_7-\text{C}(\text{O})-\text{O}-\text{R}_1$  where  $\text{R}_1$  is  $\text{C}_{2-12}$  alkyl, benzyl, or  $\text{C}_{2-12}$  alkoxyalkyl;

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B. alkyl ethers/esters of the formula  $\text{R}_2-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{O}-\text{R}_1$  where  $\text{R}_1$  is alkyl or  $-\text{C}(\text{O})$ -alkyl,  $\text{R}_2$  is alkyl and  $n$  is 2 to 100; or where  $\text{R}_1$  is hydrogen and either:  $\text{R}_2$  is alkylphenyl where the alkyl is  $\text{C}_{2-12}$  alkyl, and  $n$  is 1 to 100; or  $\text{R}_2$  is  $\text{CH}_3-(\text{CH}_2)_{10}-\text{C}(\text{O})-$  and  $n$  is 5, 10, or 15; or  $\text{R}_2$  is  $\text{CH}_3-(\text{CH}_2)_7\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{C}(\text{O})-$  and  $n$  is 5 or 15;

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C. epoxy derivatives of the formula  $\text{CH}_3-(\text{CH}_2)_n-\text{A}-(\text{CH}_2)_n-\text{R}$  in which the A is an alkene containing one or more double bonds (i.e. unsaturated fatty acids),  $n$  is 1 to 25 and R is  $\text{C}_{2-15}$  alkyl; or epoxy derivatives of triglycerides containing one or more double bonds per fatty acid chain with chain lengths from  $\text{C}_6$ -26.

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D. substituted fatty acids selected from palmitates, stearates, oleates, ricinoleates or laurates; and

- E. polymeric esters of the formula  $-O-C(O)-R_1-C(O)-O-R_2-O-$  in which  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene, or  $R_2$  may be derived from a diol.

5 5. The method of claim 4 wherein the polymeric ester is selected from glutaric polyesters having molecular weights from 2000 to 20,000, adipic polyesters having a molecular weight from 200 to 20,000, succinic polyesters, sebacic polyesters having a molecular weight from 4000 to 10,000, lactone copolymers of the formula  $[-(O-C(O)-R_1-C(O)-O-R_2-O)]_m-[(C(O)-R_3-O)]_n$  where  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkylene, or  $R_2$  may be derived from a diol, and  $R_3$  is  $-(CH_2)_5-$  (based on caprolactone), polyesters of mixed adipic, glutaric and succinic acids, polycaprolactone triol.

6. The method of claim 4 wherein the polymeric ester is poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,3-butylene glycol adipic acid) unterminated, poly(1,3-butylene glycol adipic acid) unterminated, poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2 ethylhexanol, poly(1,3-butylene glycol adipic acid) terminated with mixed fatty acids, poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,4-butylene glycol adipic acid), or poly(1,4-butylene glycol-co-ethylene glycol adipic acid).

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7. The method of claim 4 wherein the shaped object is a blown film.

8. A shaped object produced according to any one of claims 4-7.

# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/US 98/22753

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C08K5/00 C08K5/12 C08K5/11 C08K5/15 C08L67/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08K C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 28061 A (ZENECA LTD ;HAMMOND TIMOTHY (GB); LIGGAT JOHN JAMIESON (GB); MONTA) 8 December 1994 cited in the application	1-6,8
Y	see page 10, line 13-28; claims 1,2,4-7,10,11,14,16,18; example 3 ---	7
Y	EP 0 736 563 A (SAFTA SPA) 9 October 1996 cited in the application see examples 1-3 ---	7
X	WO 94 11445 A (ZENECA LTD ;HAMMOND TIMOTHY (GB); BAL JASBINDER SINGH (GB)) 26 May 1994 see example 5 ---	8
-/-		
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">18 February 1999</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">03/03/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">Rodriguez, L</div>

# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/US 98/22753

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 94 28070 A (ZENECA LTD ;LIGGAT JOHN JAMIESON (GB)) 8 December 1994 see page 6, line 4-14; claims 1,5,6 -----</p>	1-8

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Information on patent family members

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